Supporting Information for

Asymmetric seven-/eight-step spin-crossover in a three-dimensional Hofmann-type metal-organic framework

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Table S1. Spin transition temperatures from magnetic data and exothermic/endothermic peaks in DSC.

	Scan rate	Mode	step							
	K min^{-1}		**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
$\chi_M T$	0.5	$T_c\downarrow$	181	174	163	157	125	113	103	—
		$T_c\uparrow$	182	177	172	168	151	145	120	99
DSC	10	$T_c\downarrow$	182	174	162	159	124	118	102	—
		$T_c\uparrow$	183	177	173	168	145	—	123	105
	2	$T_c\downarrow$	181	173	162	158	124	108	—	—
		$T_c\uparrow$	183	177	172	167	149	146	121	106

Table S2. The HS:LS ratios, $\chi_M T$ (cm^3 K mol^{-1}) and γ_{HS}[a] values of the asymmetric seven/eight-step spin transition with eleven states in the cooling and warming modes.

state	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
HS:LS↓	1:0	9:1	3:1	—	2:1	1:1	—	3:7	1:4	—	0:1
$\chi_M T\downarrow$	3.57	3.23	2.71	—	2.41	1.85	—	1.16	0.81	—	0.12
$\gamma_{HS}\downarrow$	1.0	0.90	0.75		0.66	0.50		0.30	0.2		0
HS:LS↑	1:0	9:1	3:1	7:3	—	1:1	2:3	3:7	—	1:39	0:1
$\chi_M T\uparrow$	3.57	3.23	2.71	2.54	—	1.87	1.51	1.16	—	0.21	0.12
$\gamma_{HS}\uparrow$	1	0.90	0.75	0.70		0.51	0.40	0.30		0.026	0

[a] $\gamma_{HS} = (\chi - \chi_{LS})/(\chi_{HS} - \chi_{LS})$, where χ_{HS} and χ_{LS} are 3.57 and 0.12 cm^3 K mol^{-1}, respectively.

Table S3. Crystal data and structural refinement for **1Au** at different temperatures in the cooling mode.

Temperature/*K*	85(2)	109(2)	121(2)	143(2)	161(2)	168(2)	178(2)
chemical formula	$C_{24}H_{30}Au_2FeN_{12}O_3$	$C_{48}H_{60}Au_4Fe_2N_{24}O_6$	$C_{96}H_{120}Au_8Fe_4N_{48}O_{12}$	$C_{48}H_{60}Au_4Fe_2N_{24}O_6$	$C_{48}H_{60}Au_4Fe_2N_{24}O_6$	$C_{96}H_{120}Au_8Fe_4N_{48}O_{12}$	$C_{48}H_{60}Au_4Fe_2N_{24}O_6$
*M*r	984.38	1968.76	3937.52	1968.76	1968.76	3937.52	1968.76
crystal system	monoclinic	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
space group	*C*2/*c*	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	31.6317(12)	15.8341(16)	30.0968(12)	16.0665(15)	16.1959(3)	31.0145(8)	16.4567(11)
b/Å	12.7723(5)	12.8227(13)	12.8222(5)	12.8303(13)	12.8342(3)	12.8404(3)	12.8426(9)
c/Å	15.7074(4)	17.0691(18)	17.0738(7)	17.0485(17)	17.0951(4)	17.0864(4)	17.1057(12)
α/°	90	111.993(3)	68.1250(10)	111.797(3)	111.9735(17)	68.053(2)	112.009(2)
β/°	113.5720(10)	68.555(3)	79.568(2)	68.931(3)	69.1649(17)	79.568(2)	69.760(2)
γ/°	90	89.991(3)	77.8270(10)	89.988(3)	89.9956(17)	78.083(3)	89.949(2)
V/Å^3	5816.4(4)	2953.0(5)	5938.7(4)	3008.5(5)	3043.23(12)	6134.7(3)	3109.2(4)
Z	8	2	2	2	2	2	2
μ(Mo Kα)/mm^{-1}	20106	77872	78757	73519	53664	108522	76866
reflns collected	6167	13679	26182	13979	15877	32037	14422
indep reflns	0.0343	0.0883	0.0433	0.0897	0.0587	0.0679	0.0743
R_{int}	0.0323	0.0775	0.0801	0.1187	0.0650	0.1028	0.0384
R_1[a]($I > 2\sigma(I)$)	0.0743	0.1741	0.1686	0.2630	0.1257	0.1842	0.0860
wR_2[b](all data)	0.0785	0.1877	0.1779	0.2730	0.1330	0.2071	0.0959
GOF	1.043	1.136	1.164	1.262	1.223	1.103	1.024

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; [b] $wR_2 = \{[\sum w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

Table S4. Crystal data and structural refinement for **1Au** at different temperatures in the warming mode.

Temperature/*K*	105(2)	134(2)	158(2)	170(2)	174(2)	180(2)	240(2)
chemical formula	$C_{48}H_{60}Au_4Fe_2N_{24}O_6$	$C_{96}H_{120}Au_8Fe_4N_{48}O_{12}$	$C_{48}H_{60}Au_4Fe_2N_{24}O_6$	$C_{96}H_{120}Au_8Fe_4N_{48}O_{12}$	$C_{96}H_{120}Au_8Fe_4N_{48}O_{12}$	$C_{48}H_{60}Au_4Fe_2N_{24}O_6$	$C_{24}H_{30}Au_2FeN_{12}O_3$
*M*r	1968.76	3937.52	1968.76	3937.52	3937.52	1968.76	984.38
crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a/Å	15.8694(3)	30.1367(18)	16.0777(9)	30.948(2)	31.028(2)	16.4434(10)	31.8296(12)
b/Å	12.7869(3)	12.8338(8)	12.8480(8)	12.8483(10)	12.8539(9)	12.8355(8)	12.8950(5)
c/Å	17.0710(4)	17.0959(10)	17.0631(10)	17.1223(13)	17.1305(12)	17.1073(11)	16.4738(6)
α/°	111.9669(19)	67.9813(19)	111.6978(18)	67.991(2)	67.964(2)	112.050(2)	90
β/°	68.5105(13)	79.4822(19)	68.8685(17)	91.517(2)	79.519(2)	69.750(2)	112.0410(10)
γ/°	90.0188(12)	77.8143(19)	90.0458(19)	78.046(2)	78.084(2)	89.9829(19)	90
V/Å^3	2951.50(12)	5952.6(6)	3018.8(3)	6134.4(8)	6155.5(7)	3104.3(3)	6267.4(4)
Z	2	2	2	2	2	2	8
μ(Mo Kα)/mm^{-1}	10.451	10.364	10.218	10.057	10.023	9.937	9.844
reflns collected	49671	89478	38309	187272	188005	79130	33434
indep reflns	15035	27215	13728	28187	28292	14277	7720
R_{int}	0.1106	0.0931	0.0703	0.0532	0.0516	0.1271	0.0530
R_1[a]($I > 2\sigma(I)$)	0.0641	0.0834	0.0823	0.0786	0.0848	0.0755	0.0355
wR_2[b](all data)	0.1552	0.1912	0.1967	0.1568	0.1728	0.2077	0.0849
GOF	1.054	1.077	1.194	1.134	1.158	1.127	1.057

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; [b] $wR_2 = \{[\sum w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

Table S5. Selected structural parameters for **1Au** at different temperatures in the cooling mode.

Parameter	85 K	109 K	121 K	143 K	161 K	168 K	178 K
<Fe–N>[a]	1.965(5)	<Fe1–N> 1.999(15)	<Fe1–N> 1.990(13)	<Fe1–N> 1.998(2)	<Fe1–N> 2.080(9)	<Fe1–N> 2.111(19)	2.154(6)
		<Fe2–N> 2.012(15)	<Fe2–N> 1.970(12)	<Fe2–N> 2.123(2)	<Fe2–N> 2.106(9)	<Fe2–N> 2.078(19)	2.154(6)
			<Fe3–N> 1.986(14)			<Fe3–N> 2.093(15)	
			<Fe4–N> 2.119(15)			<Fe4–N> 2.177(15)	
Au···Au[b]	3.1883(5)	3.2028(10)	3.2026 (10)	3.2141(15)	3.2292(6)	3.2481(11)	3.2477(5)
	3.0160(4)	3.0269(9)	3.2138 (9)	3.0361(14)	3.0413(5)	3.2075(13)	3.0598(4)
			3.0212 (8)			3.0490(11)	
			3.0321 (9)			3.0467(10)	
Fe···Fe[c]	14.5766(5)	14.6405(16)	14.6039(5)	14.7179(15)	14.7782(4)	14.7782(6)	14.8917(10)
		14.6404(16)	14.6116(5)	14.7186(15)	14.7803(4)	14.7805(6)	14.890(1)
			14.7243(5)			14.8517(6)	
			14.7216(5)			14.8496(6)	
Fe···Fe[d]	10.1219(2)	10.1850(8)	10.1486(3) 10.2645(3)	10.2711(8)	10.3276(2)	10.3439(4) 10.3306(4)	10.4463(5)
	10.1229(2)	10.1917(8)	10.1379(3) 10.2878(3)	10.2825(8)	10.3280(2)	10.3159(4) 10.3233(4)	10.4395(5)
		10.1884(8)	10.1510(3) 10.2796(3)	10.2918(8)	10.3373(2)	10.4076(4) 10.4097(4)	10.4375(5)
		10.1848(8)	10.1419(3) 10.2947(3)	10.2762(8)	10.3369(2)	10.4121(4) 10.4384(4)	10.4262(5)
ΣFe[e]	19.3(2)	ΣFe1 18.5(5)	ΣFe1 21.1(5)	ΣFe1 19.3(9)	ΣFe1 20.1(3)	ΣFe1 22.8(6)	ΣFe1 20.2(2)
		ΣFe2 22.5(5)	ΣFe2 18.3(5)	ΣFe2 19.8(8)	ΣFe2 20.6(3)	ΣFe2 18.4(7)	ΣFe2 19.1(2)
			ΣFe3 19.8(5)			ΣFe3 21.3(7)	
			ΣFe4 19.7(5)			ΣFe4 22.0(6)	

Fe–N–C[f]	172.1(5)	Fe1–N–C 171.3(13) Fe2–N–C 171.7(13)	Fe1–N–C 172.0(13) Fe2–N–C 172.2(13) Fe3–N–C 171.6(13) Fe4–N–C 169.8 (14)	Fe1–N–C 171.0(2) Fe2–N–C 169.5(2)	Fe1–N–C 169.7(9) Fe2–N–C 169.7(9)	Fe1–N–C 169.5(17) Fe2–N–C 168.4(19) Fe3–N–C 168.7(17) Fe4–N–C 169.3(14)	Fe1–N–C 168.0(6) Fe2–N–C 167.8(6)
θ[g]	78.232(8)	78.025(5) 77.979(5)	78.404(22) 78.375(22) 77.201(23) 77.102(1)	77.160(4) 77.280(4)	76.791(1) 76.788(5)	76.789(6) 76.945(6) 76.168(6) 76.025(6)	75.945(1) 75.927(1)
dihedral angle[h]	1.693/21.962; 20.296	1.101/22.338; 21.248 2.684/24.542; 21.963	1.237/22.617; 21.446 1.641/22.383; 20.737 2.461/27.750; 25.375 0.634/22.938; 23.293	0.798/23.037; 23.778 3.015/28.784; 25.858	0.635/26.332; 26.276 0.595/25.218; 25.295	1.2224/26.209; 27.337 0.628/26.027; 25.693 1.277/28.512; 27.465 1.573/26.431; 27.581	1.437/27.812; 28.890 1.547/27.813;28.9 42
dihedral angle[i]	5.744	6.312 7.502	7.282 6.067 4.825 8.443	7.788 9.690	7.694 8.461	8.919 9.568 8.865 9.666	9.875 9.804

[a]The average Fe–N bond lengths (Å); [b]The argentophilic interactions (Å); [c]The Fe···Fe distance (Å) linked by 4-abpt; [d]The Fe···Fe distance (Å) linked by $[Ag(CN)_2]^-$; [e]Octahedral distortion parameters (°); [f]Average Fe–N–C angles within Hofmann layer; [g]The acute angle between neighboring Fe(II) sites within the Hofmann layer; [h]In the ligand 4-abpt, the dihedral angles between the triazole and each pyridine ring as well as the dihedral angle between the pyridine rings; [i]The dihedral angle between the up and down pyridine rings coordinated to Fe(II) site.

Table S6. Selected structural parameters for **1Au** at different temperatures in the warming mode.

Parameter	105 K	134 K	158 K	170 K	174 K	180 K	240 K
<Fe–N>[a]	<Fe1–N> 1.997(9)	<Fe1–N> 2.000(16)	<Fe1–N> 1.992(14)	<Fe1–N> 2.112(14)	<Fe1–N> 2.125(15)	<Fe1–N> 2.158(13)	2.173(5)
	<Fe2–N> 2.015(9)	<Fe2–N> 1.962(14)	<Fe2–N> 2.141(14)	<Fe2–N> 2.030(14)	<Fe2–N> 2.053(17)	<Fe2–N> 2.158(14)	
		<Fe3–N> 2.001(16)		<Fe3–N> 2.117(14)	<Fe3–N> 2.109(16)		
		<Fe4–N> 2.114(17)		<Fe4–N> 2.168(13)	<Fe4–N> 2.180(14)		
Au···Au[b]	3.2004(6)	3.2100(12)	3.2222(10)	3.2357(11)	3.2435(11)	3.2428(9)	3.2548(5)
	3.0219(5)	3.2177(11)	3.0392(9)	3.0403(10)	3.2297(12)	3.0622(8)	3.0638(4)
		3.0244(10)		3.2339(10)	3.0456(11)		
		3.0319(12)		3.0549(9)	3.0564(9)		
Fe···Fe[c]	14.6436(8)	14.6296(7)	14.7381(9)	14.7742(9)	14.7868(8)	14.8864(27)	14.9245(10)
	14.6407(8)	14.7290(7)	14.7354(9)	14.7831(9)	14.7964(8)	14.8870(27)	
		14.6408(7)		14.8717(9)	14.8966(8)		
		14.7220(7)		14.8646(9)	14.8845(8)		
Fe···Fe[d]	10.1872(3)	10.1595(5)	10.1656(4)	10.2995(5)	10.4430(6)	10.4112(5)	10.4569(5)
	10.1923(3)	10.1590(5)	10.1576(4)	10.3026(5)	10.4256(6)	10.4021(5)	10.4636(5)
	10.1909(3)	10.2604(5)	10.2927(5)	10.4256(5)	10.2995(6)	10.3214(5)	
	10.1895(3)	10.2723(5)	10.2955(5)	10.4430(5)	10.3026(6)	10.3099(5)	
ΣFe[e]	ΣFe1 21.0(4)	ΣFe1 16.3(6)	ΣFe1 17.1(6)	ΣFe1 22.0(5)	ΣFe1 22.6(6)	ΣFe1 19.0(5)	ΣFe1 19.6(19)
	ΣFe2 23.2(3)	ΣFe2 16.9(6)	ΣFe2 18.6(6)	ΣFe2 20.3(5)	ΣFe2 19.9(6)	ΣFe2 21.6(5)	
		ΣFe3 16.5(7)		ΣFe3 21.3(5)	ΣFe3 23.6(6)		
		ΣFe4 21.7(6)		ΣFe4 23.0(5)	ΣFe4 18.6(5)		

Fe–N–C[f]	Fe1–N–C 171.7(9) Fe2–N–C 172.6(10)	Fe1–N–C 171.6(15) Fe2–N–C 171.7(13) Fe3–N–C 170.4(15) Fe4–N–C 169.4(16)	Fe1–N–C 170.3(14) Fe2–N–C 169.4(15)	Fe1–N–C 170.0(14) Fe2–N–C 169.9(14) Fe3–N–C 168.6(13) Fe4–N–C 168.6(14)	Fe1–N–C 169.8(14) Fe2–N–C 169.7(16) Fe3–N–C 169.1(15) Fe4–N–C 168.7(15)	Fe1–N–C 167.6(15) Fe2–N–C 168.8(14)	168.0(5)
θ[g]	77.729(6) 77.712(6)	77.214(6) 78.311(6) 78.350(6) 77.280(6)	77.210(6) 77.306(6)	77.119(24) 76.139(22) 77.081(23) 76.103(22)	77.030(23) 77.100(22) 76.012(22) 75.932(23)	75.951(22) 75.949(22)	76.105(7)
dihedral angle[h]	0.962/23.023; 22.099 1.945/23.821; 21.954	0.715/21.802; 22.319 1.139/22.335; 21.244 2.486/27.115; 24.851 1.307/23.924; 22.781	1.597/21.270; 22.824 2.480/28.377; 26.154	0.835/25.041; 25.645 0.522/26.380; 26.513 0.683/27.520; 27.607 0.538/27.085; 26.666	1.126/25.165; 26.208 0.300/26.067; 26.272 0.779/28.301; 27.863 1.279/26.804; 27.373	2.199/28.559; 30.126 2.002/27.775; 29.141	1.206/28.063; 28.639
dihedral angle[i]	6.957 6.178	7.701 6.169 4.858 9.218	7.394 9.845	9.094 8.102 8.892 10.198	9.450 8.800 8.809 9.924	10.153 9.407	10.549

[a]The average Fe–N bond lengths (Å); [b]The argentophilic interactions (Å); [c]The Fe···Fe distance (Å) linked by 4-abpt; [d]The Fe···Fe distance (Å) linked by $[Ag(CN)_2]^-$; [e]Octahedral distortion parameters (°); [f]Average Fe–N–C angles within Hofmann layer; [g]The acute angle between neighboring Fe(II) sites within the Hofmann layer; [h]In the ligand 4-abpt, the dihedral angles between the triazole and each pyridine ring as well as the dihedral angle between the pyridine rings; [i]The dihedral angle between the up and down pyridine rings coordinated to Fe^{II} site.

Table S7. Hydrogen−bonding interactions for **1Au** at different temperatures in the cooling mode.

T	I[1]			II[2]			III[3]		
	D—H···A	**d(D···A)**	**<(DHA)**	**D—H···A**	**d(D···A)**	**<(DHA)**	**D—H···A**	**d(D···A)**	**<(DHA)**
85 K	C8−H8…N9	3.145(9)	122.6	N9−H9A...O1	2.796(14)	140.8	C20−H20B...O3[c]	2.93(3)	136.6
	C16−H16...N9	3.149(8)	116.9	N9−H9B...O2	2.921(17)	165.4	C20−H20C...O2[b]	2.61(3)	127.4
				C19−H19...N6[a]	3.055(17)	170.7	C23−H23B...O2[d]	3.29(2)	146.3
				C19−H19...N7[a]	3.525(17)	155.7	O1−H1A...O3	3.31(3)	153.9
				C20−H20A...N6[b]	3.53(2)	143.1			
				C23−H23A...N9[d]	3.261(14)	126.9			
109 K	C8−H8...N9	3.16(2)	122.8	N9−H9A...O1	2.71(3)	136.3	C95−H95A...O2[a]	3.32(6)	126.8
	C16−H16...N9	3.12(2)	117	N9−H9B...O2	2.94(4)	165.7	C20−H20B...O12[d]	3.32(8)	154.2
	C88−H88...N45	3.13(2)	117.4	N45−H45A...O10	2.68(3)	142.7	C20−H20C...O2[c]	2.79(8)	119.7
	C80−H80...N45	3.14(2)	123.5	N45−H45B...O11	2.94(4)	166.5	C92−H92C...O11[e]	2.69(7)	113.9
				C90−H90B...N44	3.48(3)	144.5	C92−H92C...O3[f]	3.18(10)	128.3
				C95−H95B...N9[a]	3.30(4)	132.9	C23−H23C...O11[g]	3.33(6)	135.7
				C19−H19...N43[b]	3.54(4)	157.4	O1−H1...O3	3.21(6)	157.6
				C19−H19...N42[b]	3.05(4)	171.1	O10−H10...O12	3.18(6)	160.3
				C20−H20A...N6[c]	3.40(5)	141.4			
				C92−H92B...N44[e]	3.30(7)	134.2			
				C23−H23B...N45[g]	3.31(4)	132.7			

	C8−H8...N9	3.14(2)	123.2	N9−H9A...O1	2.79(3)	144	C20−H20B...O6	3.01(7)	127.3
	C16−H16...N9	3.17(2)	116	N9−H9B...O2	2.96(3)	163.1	C20−H20C...O2[c]	2.56(6)	108.7
	C32−H32...N21	3.16(2)	123.5	N21−H21A...O4	2.71(3)	142	C23−H23C...O11[d]	3.29(6)	121.8
	C40−H40...N21	3.13(2)	117.4	N21−H21B...O5	2.91(4)	163.7	C44−H44A...O9[e]	2.89(5)	131.7
	C56−H56...N33	3.17(2)	123.5	N33−H33A...O7	2.69(3)	137	C44−H44B...O7[e]	3.17(7)	119.9
	C62−H62...N38[a]	3.11(2)	114.2	N33−H33B...O8	2.91(4)	164.3	C44−H44C...O11[f]	2.56(6)	122.4
	C64−H64...N33	3.13(3)	112.9	N45−H45A...O10	2.80(3)	148.4	C47−H47B...O2	3.29(5)	156.1
	C80−H80...N45	3.11(2)	123.2	N45−H45B...O11	2.98(4)	163.9	C68−H68B...O12[h]	2.91(8)	146.7
	C88−H88...N45	3.16(2)	116.9	C19−H19...N18[b]	3.08(3)	165.6	C68−H68C...O8[i]	2.69(6)	126.3
121 K				C19−H19...N19[b]	3.54(3)	162.6	C68−H68A...O10[h]	3.04(6)	104.9
				C20−H20A...N6[c]	3.47(4)	129.3	C71−H71C...O5[j]	3.29(5)	132.2
				C23−H23C...N45[d]	3.21(4)	147.2	C92−H92B...O1[k]	3.14(7)	106
				C42−H42C...N20	3.52(3)	150.8	C92−H92C...O5[f]	2.68(6)	125
				C43−H43...N6[c]	3.09(3)	154.6	O4−H4...O6	3.06(5)	160.9
				C43−H43...N7[c]	3.55(3)	172.1	O7−H7...O9	3.09(4)	161
				C44−H44B...N42[f]	3.49(4)	133.7	O10−H10...O12	3.23(7)	147.8
				C67−H67...N42[g]	3.14(3)	164.1			
				C67−H67...N43[g]	3.59(3)	165.4			
				C71−H71B...N21[j]	3.36(3)	132			
				C91−H91...N30[f]	3.10(4)	143.1			

				C91−H91...N31[f]	3.53(3)	165			
				C95−H95B...N33[l]	3.37(4)	120.1			
143 K	C8−H8...N9	3.15(4)	123.3	N9−H9A...O1	2.66(6)	145.4	C20−H20A...O10[e]	3.08(11)	118.8
	C14−H14...N38[b]	3.10(3)	114.8	N9−H9B...O2	3.01(8)	166.7	C20−H20B...O12[e]	3.17(11)	136.5
	C15−H15...N16[c]	3.15(4)	110.7	N45−H45A...O10	2.69(5)	147.9	C20−H20C...O2[f]	2.78(10)	119.2
	C16−H16...N9	3.14(4)	112.6	N45−H45B...O11[a]	3.02(8)	164.7	C92−H92A...O1[d]	3.04(11)	112
	C86−H86...N2	3.05(4)	110.6	C19−H19...N42[d]	3.20(11)	166.6	C92−H92B...O11[a]	2.71(10)	116.5
	C88−H88...N45	3.13(4)	116.3	C90−H90A...N44	3.44(8)	135.8	C92−H92C...O3[d]	3.09(9)	150.4
	C80−H80...N45	3.11(4)	124.3	C91−H91...N6[g]	3.04(11)	163.8	C23−H23C...O11[d]	3.35(10)	175.8
				C91−H91...N7[g]	3.54(10)	163.5	O1−H1...O3	3.26(8)	143.8
				C92−H92A...N42	3.46(8)	138.4	O10−H10...O12	3.07(9)	153.5
161 K	C8−H8...N9	3.142(14)	123.8	N9−H9A...O1	2.70 (3)	145	C20−H20B...O2[d]	2.64(3)	118.2
	C14−H14...N38[a]	3.100(14)	113	N9−H9B...O2	3.03(2)	165.4	C20−H20C...O12[e]	3.09(4)	147.1
	C15−H15...N16[b]	3.137(15)	111	N45−H45A...O10	2.80(2)	152.2	C23−H23C...O11[b]	3.37(4)	137.4
	C16−H16...N9	3.135(15)	115.6	N45−H45B...O11	3.09(2)	168.4	C93−H93A...O11[h]	2.76(4)	133.8
	C80−H80...N45	3.143(15)	123.9	C19−H19...N42[c]	3.19(2)	154.8	C93−H93B...O1[i]	3.02(4)	114.2
	C86−H86...N2	3.072(14)	112.9	C20−H20A...N6[d]	3.49(2)	142.5	C95−H95C...O3[i]	2.91(4)	134.7
	C88−H88...N45	3.128(16)	116.3	C23−H23B...N45[b]	3.36(2)	131.6	O1−H1...O3	3.13(4)	155.8
				C92−H92B...N44	3.53(2)	144.2	O10−H10...O12	3.25(5)	147.1
				C95−H95B...N9[f]	3.38(5)	142			

				C91−H91...N6[g]	3.18(7)	122.6			
				C91−H91...N7[g]	3.54(4)	149.7			
168 K	C8−H8...N9	3.07(3)	123.2	N9−H9A...O1	2.74(4)	148.8	C20−H20A...O6	3.01(9)	140.6
	C14−H14...N14[a]	3.02(3)	114.3	N9−H9B...O2	3.03(4)	165	C20−H20B...O2[d]	2.64(6)	127.5
	C16−H16...N9	3.15(3)	116	N21−H21A...O4	2.85(4)	144.9	C44−H44A...O9[e]	2.90(8)	129.8
	C32−H32...N21	3.17(3)	122	N21−H21B...O5	3.03(5)	164.9	C44−H44C...O11[f]	2.60(7)	115.8
	C38−H38...N26[a]	3.10(3)	113.3	N33−H33A...O7	2.79(3)	131.9	C68−H68A...O8[h]	2.70(6)	114.5
	C40−H40...N21	3.09(4)	116.6	N33−H33B...O8	3.07(4)	165.6	C68−H68C...O12[i]	3.09(7)	150.8
	C56−H56...N33	3.15(3)	124.4	N45−H45A...O10	2.77(5)	154.1	C92−H92A...O5[f]	2.68(6)	124.7
	C62−H62...N38[b]	3.18(2)	115.3	N45−H45B...O11	3.06(5)	165.9	C92−H92B...O3[j]	3.06(7)	143
	C64−H64...N33	3.13(3)	113.3	C19−H19...N18[c]	3.20(4)	162.8	C92−H92C...O1[j]	3.01(7)	110.8
	C80−H80...N45	3.09(2)	125.5	C20−H20C...N6[d]	3.50(4)	139.9	C95−H95B...O8[k]	3.56(8)	141.2
	C86−H86...N2	3.07(2)	115.6	C43−H43...N6[d]	3.22(5)	145.6	O1−H1...O3	3.01(6)	154.3
	C88−H88...N45	3.14(3)	114.1	C67−H67...N42[g]	3.24(5)	141.4	O4−H4...O6	3.06(7)	151.9
				C68−H68B...N30[h]	3.48(4)	146.7	O7−H7...O9	3.07(7)	172.4
				C91−H91...N30[f]	3.23(4)	150.2			
				C92−H92C...N18[f]	3.49(4)	143.9			
178 K	C8−H8...N9	3.116(9)	124.4	N9−H9A...O1	2.786(16)	147.8	C20−H20A...O12[c]	2.98(3)	142
	C14−H14...N38[a]	3.144(9)	116.4	N9−H9B...O2	3.057(17)	166.4	C20−H20B...O2[d]	2.70(2)	126.9
	C16−H16...N9	3.127(10)	113.9	N45−H45A...O10	2.780(15)	151.3	C20−H20C...O10[c]	3.02(2)	114.2

C86−H86...N2	3.146(9)	117.1	N45−H45B...O11	3.060(18)	165.8	C92−H92A...O1[f]	3.01(2)	109.8
C88−H88...N45	3.126(10)	114.5	C19−H19...N42[b]	3.211(18)	157.7	C92−H92B...O11[g]	2.68(2)	134.3
C80−H80...N45	3.131(9)	123.8	C91−H91...N6[e]	3.196(19)	159.6	C92−H92C...O3[f]	2.95(4)	142.7
						C23−H23C...O11[h]	3.48(3)	163.6
						O1−H1...O3	3.10(4)	150.9
						O10−H10...O12	3.08(3)	154.3

[1] Intramolecular hydrogen bonds in the framework; [2] Hydrogen − bonding interactions between host and guest; [3] Hydrogen − bonding interactions between guests.

Symmetry codes: [1] at 85 K: (a) −x+1/2, y+1/2, −z+3/2; (b) −x+1/2, −y+1/2, −z+2; (c) x, −y+1, z+1/2; (d) x, −y+1, z−1/2; [2] at 109 K: (a) x+1, y−1, z−1; (b) −x+1, −y+1, −z+1; (c) −x, −y+1, −z+2; (d) x−1, y+1, z+1; (e) −x+1, −y, −z; (f) x, y−1, z−1; (g) x, y+1, z+1; [3] at 121 K: (a) x+1, y−1, z; (b) −x+1,−y+1,−z+1; (c) −x+1, −y+2, −z+1; (d) x, y−1, z+1; (e) x, y+1, z; (f) −x+1, −y+2, −z; (g) −x+1, −y+1, −z; (h) x+1, y−2, z; (i) −x+2, −y, −z; (j) x, y−1, z; (k) x, y+1, z−1; (l) x−1, y+2, z; [4] at 143 K: (a) −x+1,−y,−z; (b) x−1,y,z+1; (c) x,y+1,z+1; (d) −x+1,−y+1,−z+1; (e) x−1,y+1,z+1; (f) −x,−y+1,−z+2; (g) x,y,z−1; [5] at 161 K: (a) x+1,y,z−1 (b) x, y−1, z−1; (c) −x+1, −y−1, −z−1; (d) –x+2, −y−1, −z−2; (e) x+1, y−1, z−1; (f) x−1, y+1, z+1; (g) −x+1, −y, −z−1; (h) −x+1, −y, −z; (i) x, y+1, z+1; [6] at 168 K: (a) x, y, z+1; (b) x+1, y−1, z; (c) −x+1, −y+1, −z+1; (d) −x+1, −y+2, −z+1; (e) x, y+1, z; (f) −x+1, −y+2, −z; (g) −x+1, −y+1, −z; (h) −x+2, −y, −z; (i) x+1, y−2, z; (j) x, y+1, z−1; (k) x−1, y+2, z; [7] at 178 K: (a) x-1,y,z+1; (b) -x+1,-y+1,-z+1; (c) x-1,y+1,z+1; (d) -x,-y+1,-z+2; (e) -x+1,-y,-z+1; (f) x,y-1,z-1; (g) -x+1,-y,-z; (h) x,y+1,z+1;

Table S8. Hydrogen−bonding interactions for **1Au** at different temperatures in the warming mode.

T	I[1]			II[2]			III[3]		
	D—H···A	**d(D···A)**	**<(DHA)**	**D—H···A**	**d(D···A)**	**<(DHA)**	**D—H···A**	**d(D···A)**	**<(DHA)**
105 K	C8−H8...N9	3.178(14)	122	N9−H9A...O1	2.671(19)	139	C95−H95A...O2[b]	3.31(3)	126.9
	C14−H14...N38[a]	3.005(14)	110.6	N9−H9B...O2	2.96(3)	164.6	C20−H20A...O2[d]	2.55(4)	128.9
	C16−H16...N9	3.141(14)	117.3	N45−H45A...O10	2.79(2)	147.4	C20−H20C...O12[e]	2.94(4)	138.6
	C88−H88...N45	3.144(14)	115.3	N45−H45B...O11	2.95(2)	165.3	C92−H92B...O11[g]	2.68(4)	141.6
	C80−H80...N45	3.146(14)	123.4	C95−H95B...N9[b]	3.28(2)	132.2	C92−H92C...O3[h]	2.91(4)	143.4
				C19−H19...N43[c]	3.60(2)	172.7	C23−H23C...O11[i]	3.16(3)	129.3
				C19−H19...N42[c]	3.15(2)	155.2	O1−H1...O3	3.17(4)	156.1
				C20−H20B...N6[d]	3.47(3)	147	O10−H10...O12	3.37(4)	151.8
				C91−H91...N6[f]	3.12(3)	147.2			
				C91−H91...N7[f]	3.55(2)	167.4			
				C92−H92A...N42[g]	3.49(3)	147			
				C23−H23C...N45[i]	3.28(2)	134.2			
				C18−H18B...N8	3.555(18)	149.9			
134 K	C8−H8...N9	3.11(2)	123	N9−H9A...O1	2.77(3)	143.7	C20−H20A...O6	2.97(7)	132.5
	C16−H16...N9	3.14(3)	118.1	N9−H9B...O2	2.92(4)	163.6	C20−H20B...O2[c]	2.69(6)	110.4
	C32−H32...N21	3.16(3)	123.5	N21−H21A...O4	2.88(4)	139.4	C20−H20C...O4	3.23(8)	118.6
	C40−H40...N21	3.13(3)	118.3	N21−H21B...O5	2.93(5)	167.2	C44−H44A...O9[e]	3.05(6)	131.2
	C56−H56...N33	3.20(3)	123.1	N33−H33A...O7	2.67(3)	134.7	C44−H44B...O7[e]	3.24(7)	120.3

	C62−H62...N38[a]	3.13(3)	113.8	N33−H33B...O8	3.01(5)	165.6	C44−H44C...O11[f]	2.64(6)	124.9
	C64−H64...N33	3.15(3)	113.9	N45−H45A...O10	2.80(4)	145.1	C47−H47B...O2	3.22(6)	154.1
	C80−H80...N45	3.10(3)	123.1	N45−H45B...O11	2.96(4)	164.9	C68−H68A...O12[h]	3.05(8)	144.2
	C86−H86...N2	3.01(2)	113.5	C19−H19...N18[b]	3.07(4)	139.4	C68−H68B...O8[i]	2.74(6)	127.9
	C88−H88...N45	3.17(3)	115.6	C19−H19...N19[b]	3.48(4)	164.6	C71−H71A...O5[j]	3.28(8)	123.5
				C23−H23C...N45[d]	3.13(4)	119.9	C92−H92A...O3[k]	2.97(7)	143.7
				C43−H43...N6[c]	3.11(8)	135.9	C92−H92C...O5[f]	2.81(9)	117.3
				C43−H43...N7[c]	3.49(5)	163.6	O1−H1...O3	3.36(6)	164.8
				C47−H47B...N9	3.26(3)	117	O4−H4...O6	3.26(6)	170.1
				C66−H66C...N32	3.56(3)	150.3	O7−H7...O9	3.09(6)	160.9
				C67−H67...N42[g]	3.13(4)	166.6	O10−H10...O12	3.35(7)	151.4
				C68−H68C...N30[i]	3.44(5)	148.9			
				C71−H71C...N21[j]	3.36(3)	142.5			
				C91−H91...N30[f]	3.12(4)	175.6			
				C92−H92B...N18[f]	3.39(4)	135.1			
				C95−H95A...N33[l]	3.38(4)	131.6			
	C8−H8...N9	3.15(3)	121.6	N9−H9A...O1	2.84(6)	151.8	C20−H20A...O12[d]	2.95(8)	135.6
	C14−H14...N15	3.06(2)	111.2	N9−H9B...O2	3.05(4)	168.3	C20−H20B...O2[e]	2.69(6)	129.1
158 K	C16−H16...N9	3.15(3)	114.3	N45−H45A...O10	2.82(3)	151.4	C20−H20C...O10[d]	3.09(7)	117.1
	C86−H86...N2	3.01(2)	110.7	N45−H45B...O11	3.03(4)	166.2	C92−H92A...O1[g]	3.14(7)	122.5
	C88−H88...N45	3.13(2)	117	C95−H95A...N9[b]	3.41(4)	138.1	C92−H92B...O11[h]	2.69(7)	124.5

	C80−H80...N45	3.13(3)	124.7	C19−H19...N42[c]	3.20(5)	169.9	C92−H92C...O3[g]	2.97(7)	130.2
				C91−H91...N6[f]	3.14(4)	168.9	C23−H23C...O11[i]	3.33(6)	141
				C91−H91...N7[f]	3.61(4)	160.2	O1−H1...O3	3.14(5)	157.7
				C23−H23C...N45[i]	3.38(3)	127	O10−H10...O12	2.98(7)	157.8
170 K	C8−H8...N9	3.11(3)	124.1	N9−H9A...O2	2.97(3)	162.6	C20−H20A...O8[a]	2.72(6)	127.1
	C14−H14...N14[a]	3.10(2)	113.2	N9−H9B...O1	2.70(3)	142.7	C20−H20C...O6[c]	2.90(7)	147.4
	C15−H15...N16	3.15(2)	112.6	N21−H21A...O5	3.01(3)	165.4	C44−H44B...O5[f]	2.70(5)	137.8
	C16−H16...N9	3.12(3)	115.7	N21−H21B...O4	2.82(3)	151.4	C44−H44C...O9[f]	2.98(6)	142.9
	C32−H32...N21	3.16(2)	123	N33−H33A...O8	3.03(4)	166.2	C68−H68A...O2[g]	2.73(5)	135.7
	C38−H38...N26	3.13(2)	117	N33−H33B...O7	2.82(3)	151.4	C68−H68B...O12[h]	3.16(6)	144.6
	C40−H40...N21	3.10(2)	116.8	N45−H45A...O11	3.05(4)	168.3	C92−H92A...O3[e]	2.96(6)	130.3
	C56−H56...N33	3.11(2)	122.8	N45−H45B...O10	2.84(6)	151.8	C92−H92C...O11[i]	2.71(5)	112.8
	C62−H62...N38	3.12(2)	115.1	C19−H19...N42[b]	3.20(3)	146.8	O1−H1...O3	2.94(5)	145.9
	C64−H64...N33	3.14(2)	114.8	C20−H20B...N30[a]	3.52(3)	145.6	O4−H4...O6	3.16(5)	146.7
	C80−H80...N45	3.11(3)	124.1	C23−H23A...N45[d]	3.39(3)	136.1	O7−H7...O9	3.13(5)	151.2
	C86−H86...N2	3.06(2)	111.2	C42−H42C...N20	2.51(3)	145.3	O10−H10...O12	3.26(7)	145.6
	C88−H88...N45	3.16(2)	115.8	C43−H43...N30[e]	3.10(4)	162.3			
				C43−H43...N31[e]	3.57(4)	166.4			
				C44−H44A...N18[f]	3.52(4)	146.4			
				C67−H67...N18	3.16(3)	169.6			
				C68−H68C...N6[g]	3.46(4)	142.6			

					C91−H91...N6[i]	3.16(4)	154.1			
					C91−H91...N7[i]	3.58(3)	174.3			
					C92−H92C...N44[i]	3.45(4)	133.8			
					C95−H95A...N33[h]	3.44(3)	149.9			
174 K	C8−H8...N9	3.11(3)	123.2	N9−H9A...O1	2.77(6)	151.9	C20−H20B...O2[d]	2.69(5)	154.5	
	C14−H14...N14[a]	3.08(3)	111.5	N9−H9B...O2	2.99(4)	165.1	C20−H20A...O4	3.04(5)	134.9	
	C16−H16...N9	3.14(3)	117.1	N21−H21A...O4	2.78(4)	148.1	C20−H20C...O6	2.92(7)	124.7	
	C32−H32...N21	3.16(2)	123.7	N21−H21B...O5	2.97(4)	163.7	C44−H44A...O9[f]	2.97(6)	146.7	
	C38−H38...N26[a]	3.11(3)	112.4	N33−H33A...O7	2.86(3)	147.2	C44−H44B...O7[f]	3.00(5)	112.6	
	C39−H39...N28[a]	3.14(2)	112.7	N33−H33B...O8	3.05(4)	164.7	C44−H44C...O11[g]	2.78(7)	125.2	
	C40−H40...N21	3.11(3)	114.8	N45−H45A...O10	2.72(3)	142.7	C47−H47C...O2	3.35(6)	132.7	
	C56−H56...N33	3.16(2)	124.1	N45−H45B...O11	3.07(4)	169.2	C68−H68A...O8[i]	2.69(5)	107.6	
	C62−H62...N38[b]	3.14(2)	117.5	C19−H19...N18[c]	3.17(4)	169.7	C68−H68B...O10[j]	3.14(5)	131.7	
	C64−H64...N33	3.13(3)	113.4	C20−H20A...N6[d]	3.60(5)	160.6	C68−H68C...O12[j]	3.10(7)	128.3	
	C80−H80...N45	3.14(3)	123.7	C23−H23B...N45[e]	3.45(4)	135.4	C92−H92B...O5[g]	2.68(5)	134.3	
	C86−H86...N2	3.12(2)	116.7	C43−H43...N6[d]	3.16(4)	155.8	C92−H92C...O3[l]	3.01(7)	145.2	
	C88−H88...N45	3.13(2)	115.6	C43−H43...N7[d]	3.63(4)	172.6	C95−H95A...O8[m]	3.58(6)	123.7	
				C44−H44B...N42[g]	3.47(4)	136.8	O1−H1...O3	3.16(7)	140.3	
				C67−H67...N42[h]	3.22(3)	162.2	O4−H4...O6	3.15(5)	149	
				C71−H71C...N21[k]	3.40(3)	132.8	O7−H7...O9	3.20(5)	150.3	
				C91−H91...N30[g]	3.19(4)	155	O10−H10...O12	3.04(5)	167.1	

				C91−H91...N31[g]	3.64(3)	173.5			
				C92−H92A...N18[g]	3.46(4)	149.4			
180 K	C8−H8...N9	3.12(2)	123.6	N9−H9A...O1	2.82(4)	151.1	C20−H20A...O12[c]	2.98(6)	142.1
	C14−H14...N38[a]	3.15(2)	116.5	N9−H9B...O2	3.04(4)	165.5	C20−H20B...O2[d]	2.67(5)	122.2
	C16−H16...N9	3.13(2)	115.4	N45−H45A...O10	2.76(3)	145.6	C20−H20C...O10[c]	3.16(6)	114.7
	C86−H86...N2	3.15(2)	116.6	N45−H45B...O11	3.05(4)	165	C92−H92B...O11[f]	2.67(4)	128.7
	C88−H88...N45	3.14(2)	115.4	C19−H19...N42[b]	3.18(3)	161.9	C92−H92C...O3[g]	3.05(6)	145.8
	C87−H87...N4	3.19(2)	114.4	C91−H91...N6[e]	3.19(3)	158.9	C23−H23C...O11[h]	3.52(6)	149.4
	C80−H80...N45	3.12(2)	124	C92−H92A...N42[f]	3.53(4)	146.5	O1−H1...O3	3.17(7)	147.6
							O10−H10...O12	2.92(5)	164.9
240 K	C8−H8…N9	3.128(8)	124.1	N9−H9A...O1	2.760(13)	140.7	C20−H20A...O1[c]	3.21(2)	120.9
	C14−H14...N2[a]	3.175(8)	117.4	N9−H9B...O2	3.064(18)	166.2	C20−H20B...O3[c]	3.06(2)	139.7
	C16−H16...N9	3.138(8)	114.3	C19−H19...N6[b]	3.28(2)	145.7	C20−H20C...O2[d]	2.71(2)	118.4
				C23−H23A...N9[e]	3.438(14)	133.6	O1−H1A...O3	2.96(2)	163.3

[1] Intramolecular hydrogen bonds in the framework; [2] Hydrogen−bonding interactions between host and guest; [3] Hydrogen−bonding interactions between guests.

Symmetry codes:[1] at 105 K: (a) x−1, y, z+1; (b) x+1, y−1, z−1; (c) −x+1, −y+1, −z+1; (d) −x, −y+1, −z+2; (e) x−1, y+1, z+1; (f) −x+1, −y, −z+1; (g) −x+1, −y, −z; (h) x, y−1, z−1; (i) x, y+1, z+1; [2] at 134 K: (a) x+1, y−1, z; (b) −x+1, −y+1, −z+1; (c) −x+1, −y+2, −z+1; (d) x, y−1, z+1; (e) x, y+1, z; (f) −x+1, −y+2, −z; (g) −x+1, −y+1, −z; (h) x+1, y−2, z; (i) −x+2, −y, −z; (j) x, y−1,z; (k) x, y+1, z−1; (l) x−1, y+2, z; [3] at 158K: (a) x−1, y, z+1; (b) x+1, y−1, z−1; (c) −x+1, −y+1, −z+1; (d) x−1, y+1, z+1; (e) −x, −y+1, −z+2; (f) −x+1, −y, −z+1; (g) x, y−1, z−1; (h) −x+1, −y, −z; (i) x, y+1, z+1; [4] at 170 K: (a) x, y, z−1; (b) −x+1, −y+2, −z; (c) x, y+1, z−1; (d) x, y+1, z; (e) x, y−1, z; (f) −x, −y+2, −z+1; (g) x, y, z+1; (h) −x+1, −y+1, −z+1;(i) −x+1, −y+1, −z; [5] at 174 K: (a) x, y, z+1; (b) x+1, y−1, z; (c) −x+1, −y+1, −z+1; (d) −x+1, −y+2, −z+1; (e) x, y−1, z+1; (f) x, y+1, z; (g) −x+1, −y+2, −z; (h) −x+1, −y+1, −z; (i) −x+2, −y, −z; (j) x+1, y−2, z; (k) x, y−1, z; (l) x, y+1, z−1; (m) x−1, y+2, z; [6] at 180 K: (a) x−1, y, z+1; (b) −x+1, −y+1, −z+1; (c) x−1, y+1, z+1; (d) −x, −y+1, −z+2; (e) −x+1, −y, −z+1; (f) −x+1, −y, −z; (g) x, y−1, z−1; (h) x, y+1, z+1; [7] at 240 K: (a) x+1/2, −y+1/2, z+1/2; (b) −x+1/2, y+1/2, −z+3/2; (c) x, −y+1, z+1/2; (d) –x+1/2, −y+1/2, −z+2; (e) x, −y+1, z−1/2.

Table S9. Selected structural parameters for **1Au** and **1Ag** in the HS and LS states.

Parameter	1Au(HS)	1Au(LS)	1Ag(HS)	1Ag(LS)
<Fe–N>[a]	2.173(5)	1.965(5)	2.173(3)	1.964(5)
M···M[b]	3.0638(4)	3.0160(4)	3.0533(6)	2.9902(9)
	3.2548(5)	3.1883(5)	3.2032(7)	3.1246(10)
Fe···Fe[c]	14.9245(10)	14.5766(5)	14.9362(9)	14.5699(11)
Fe···Fe[d]	10.4569(5)	10.1219(2)	10.5783(6)	10.2399(12)
	10.4636(5)	10.1229(2)	10.5691(6)	10.2400(12)
ΣFe[e]	19.62(19)	19.3(2)	15.10(11)	17.08(19)
Fe–N–C[f]	168.0(5)	172.1(5)	168.2(3)	172.8(5)
θ[g]	76.105(7)	78.232(8)	75.532(4)	77.397(7)
dihedral angle[h]	1.21/28.06; 28.64	1.69/21.96; 20.30	1.31/26.25; 27.17	1.79/20.48; 18.76
dihedral angle[i]	10.549	5.744	7.08	4.58

[a]The average Fe–N bond lengths (Å); [b]The Au···Au or Ag···Ag distances (Å); [c]The Fe···Fe distance (Å) linked by 4-abpt; [d]The Fe···Fe distance (Å) linked by $[Au(CN)_2]^-$ (or $[Ag(CN)_2]^-$); [e]Octahedral distortion parameters (°); [f]Average Fe–N–C angles within Hofmann layer; [g]The acute angle between neighboring Fe(II) sites within the Hofmann layer; [h]In the ligand 4-abpt, the dihedral angles between the triazole and each pyridine ring as well as the dihedral angle between the pyridine rings; [i]The dihedral angle between the up and down pyridine rings coordinated to Fe^{II} site.

Table S10. Selected Fe-N bond lengths [Å], N-Fe-N and Fe-N-C angles [°] for **1Au** and **1Ag** at 240 K.

Compound 1Au (HS)		**Compound 1Ag (HS)**		**difference**
Fe1−N2	2.154(5)	Fe1−N2	2.154(3)	0(5)
Fe1−N4	2.148(5)	Fe1−N4	2.142(3)	0.006(5)
Fe1−N5	2.202(5)	Fe1−N5	2.209(2)	-0.007(5)
Fe1−N10^{c}	2.221(5)	Fe1−N10^{c}	2.217(2)	0.004(5)
Fe1−N13^{d}	2.157(5)	Fe1−N13^{a}	2.159(3)	-0.002(5)
Fe1−N39^{e}	2.157(4)	Fe1−N39^{b}	2.156(3)	0.001(4)
N2−Fe1−N5	89.65(17)	N2−Fe1−N5	89.94(10)	-0.29(17)
N2−Fe1−N10^{c}	89.60(17)	N2−Fe1–N10^{c}	89.42(10)	0.18(17)
N2−Fe1−N13^{d}	91.88(18)	N2−Fe1−N13^{a}	91.38(11)	0.5(18)
N2−Fe1−N39^{e}	89.74(18)	N2−Fe1−N39^{b}	89.85(11)	-0.11(18)
N4−Fe1−N5	89.89(17)	N4–Fe1–N5	90.59(10)	-0.7(17)
N4−Fe1−N10^{c}	90.86(17)	N4–Fe1–N10^{c}	90.05(10)	0.81(17)
N4−Fe1−N13^{d}	86.88(19)	N4–Fe1–N13^{a}	87.27(11)	-0.39(19)
N4−Fe1−N39^{e}	91.51(19)	N4–Fe1–N39^{b}	91.50(11)	0.01(19)
N13^{d}–Fe1−N5	93.10(18)	N13^{a}–Fe1−N5	92.11(10)	0.99(18)
N13^{d}–Fe1−N10^{c}	86.90(17)	N13^{a}–Fe1−N10^{c}	87.76(10)	-0.86(17)
N39^{e}–Fe1−N5	87.55(17)	N39^{b}–Fe1–N5	88.22(10)	-0.67(17)
N39^{e}–Fe1−N10^{c}	92.48(18)	N39^{b}–Fe1–N10^{c}	91.93(10)	0.55(17)
Fe1−N2−C2	176.7(5)	Fe1–N2–C2	177.1(3)	-0.4(5)
Fe1−N4−C4	171.9(5)	Fe1–N4–C4	171.9(3)	0(5)
Fe1−N13^{g}–C25^{g}	159.9(5)	Fe1–N13^{a}–C25^{a}	159.2(3)	0.7(5)
Fe1−N39^{h}–C75^{h}	163.3(5)	Fe1–N39^{b}–C75^{b}	164.4(3)	-1.1(5)

Symmetry codes: [1] for **1Au**: c) x-1/2, -y+1/2, z-1/2; d) x, -y+1, z-1/2; e) x, -y, z+1/2; g) x, -y+1, z+1/2; h) x, -y, z-1/2; [2] for **1Ag**: a) x, 1-y, -1/2+z; b) x, -y, 1/2+z; c) -1/2+x, 1/2–y, –1/2+z

Table S11. Selected Hydrogen−bonding interactions for **1Au** and **1Ag** at 240 K.

T	I[1]			II[2]			III[3]		
	D—H···A	**d(D···A)**	**<(DHA)**	**D—H···A**	**d(D···A)**	**<(DHA)**	**D—H···A**	**d(D···A)**	**<(DHA)**
240 K (**1Au**)	C8−H8…N9	3.128(8)	124.1	N9−H9A...O1	2.760(13)	140.7	C20−H20A...O1[c]	3.21(2)	120.9
	C14−H14...N2[a]	3.175(8)	117.4	N9−H9B...O2	3.064(18)	166.2	C20−H20B...O3[c]	3.06(2)	139.7
	C16−H16...N9	3.138(8)	114.3	C19−H19...N6[b]	3.28(2)	145.7	C20−H20C...O2[d]	2.71(2)	118.4
				C23−H23A...N9[e]	3.438(14)	133.6	O1−H1A...O3	2.96(2)	163.3
240 K (**1Ag**)	C16−H16...N9	3.123(4)	114.9	N9−H9A...O1	2.816(7)	126.4	O1−H1A...O3	2.859(13)	173.6
	C14−H14...N2[a]	3.197(4)	115.3	N9−H9B...O2	2.870(9)	171.2	C20−H20B...O3[c]	3.231(15)	152.4
				C19−H19...N6[b]	3.269(12)	140.1	C20−H20C...O2[d]	2.92(2)	129.6

[1] Intramolecular hydrogen bonds in the framework; [2] Hydrogen-bonding interactions between host and guest; [3] Hydrogen-bonding interactions between guests. Symmetry codes **: 1Au:** (a) x+1/2, −y+1/2, z+1/2; (b) −x+1/2, y+1/2, −z+3/2; (c) x, −y+1, z+1/2; (d) –x+1/2, −y+1/2, −z+2; (e) x, −y+1, z−1/2. **1Ag:** a) x+1/2, –y+1/2, z+1/2; b) –x+1/2, y+1/2, –z+3/2; c) x, –y+1, z+1/2; d) –x+1/2, –y+1/2, –z+2

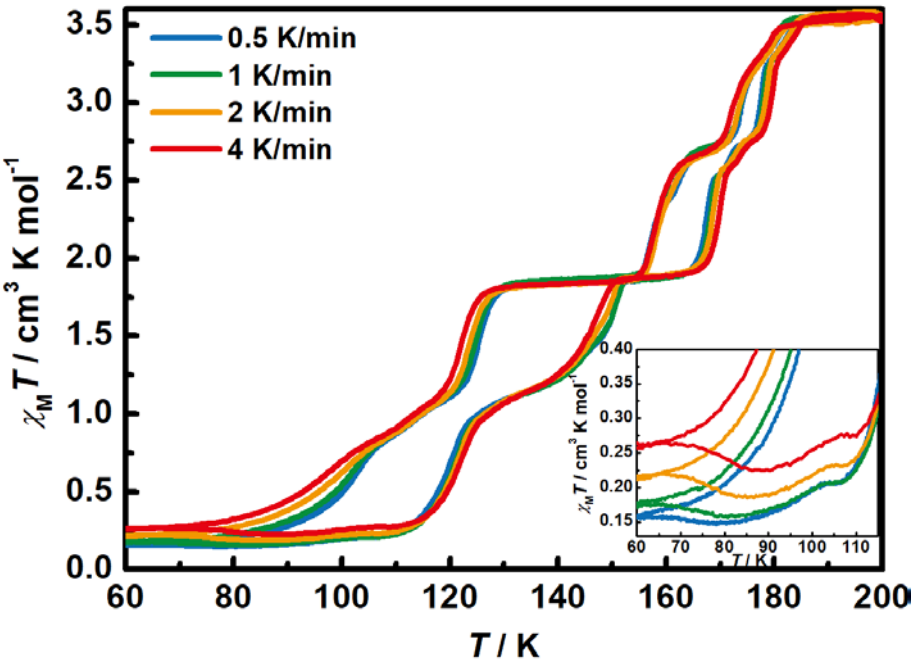


Figure S1. Variable-temperature magnetic susceptibility for **1Au** at different scan rates. The magnetic data in the range of 60-115 K is presented in the insert.

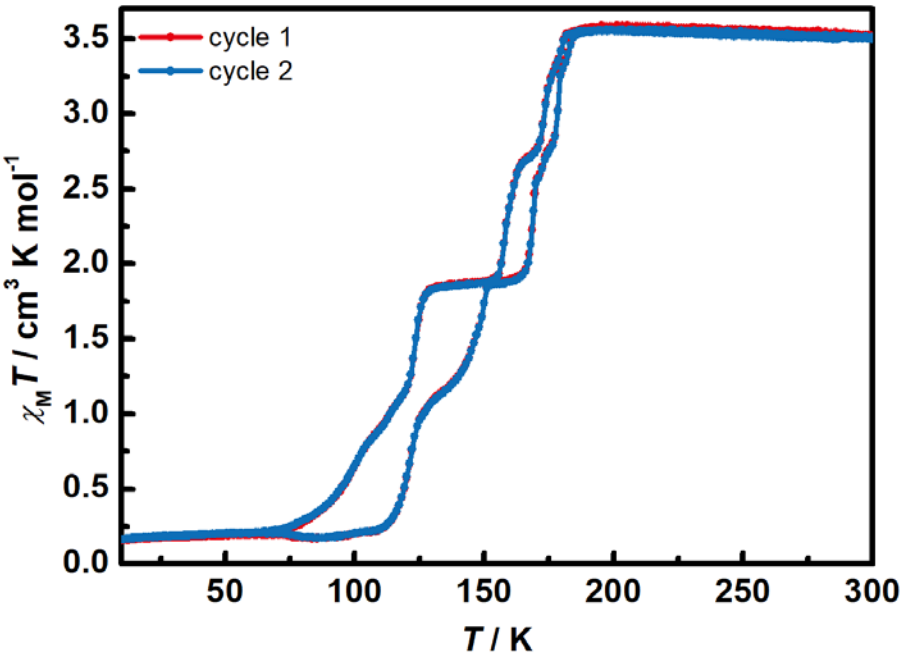


Figure S2. Variable-temperature magnetic susceptibility with two consecutive cycles for **1Au** at 2 K min^{-1}.

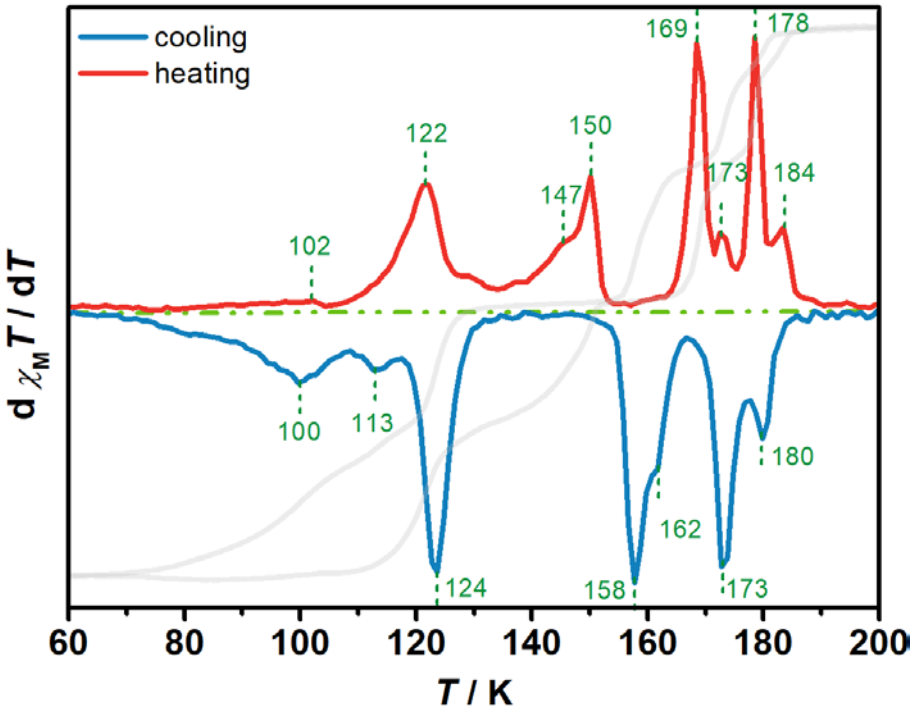


Figure S3. The first derivative curve of the magnetic susceptibility at 2 K min^{-1} for **1Au** on cooling (blue) and heating (red).

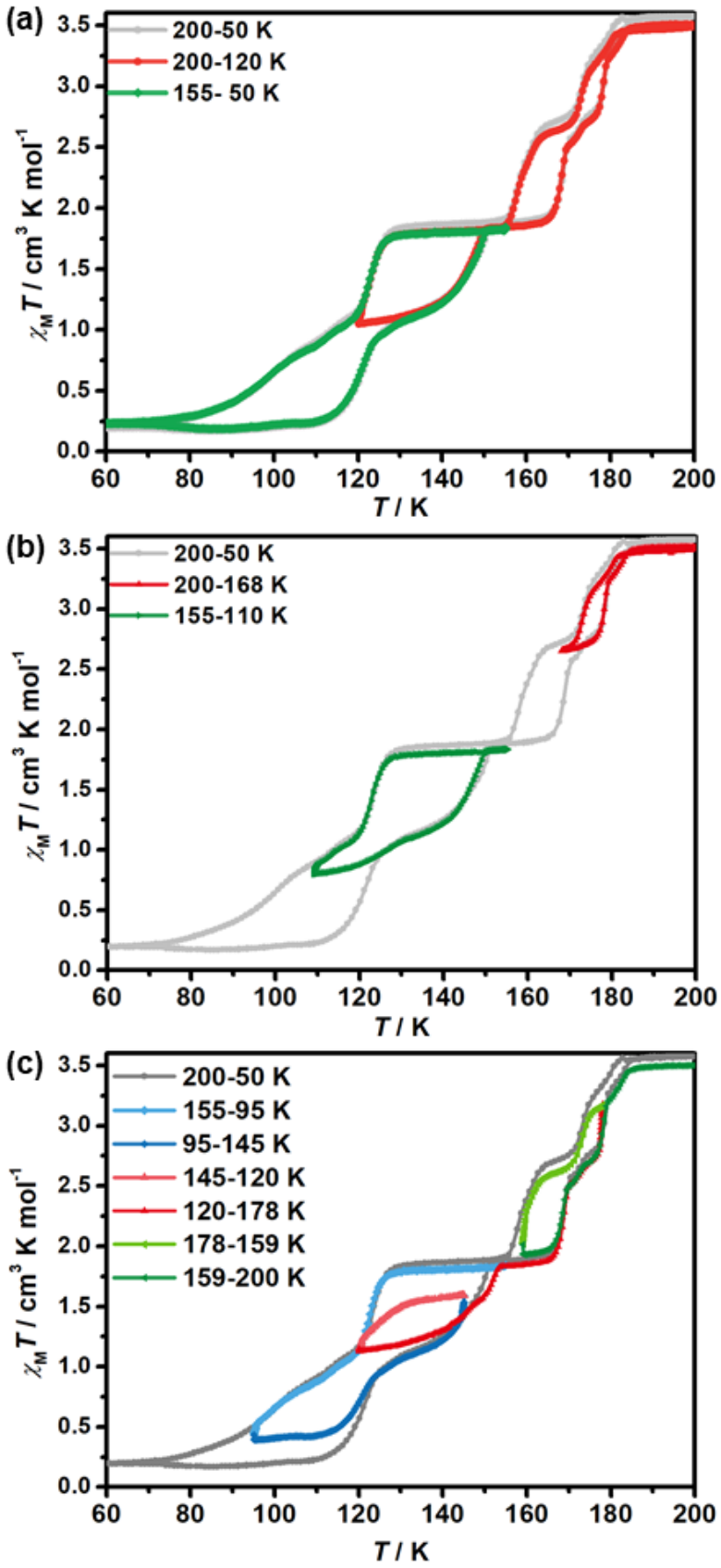


Figure S4. Variable-temperature magnetic susceptibility for **1Au** at 2 K·min^{-1} in different range of temperatures to traverse each intermediate state.

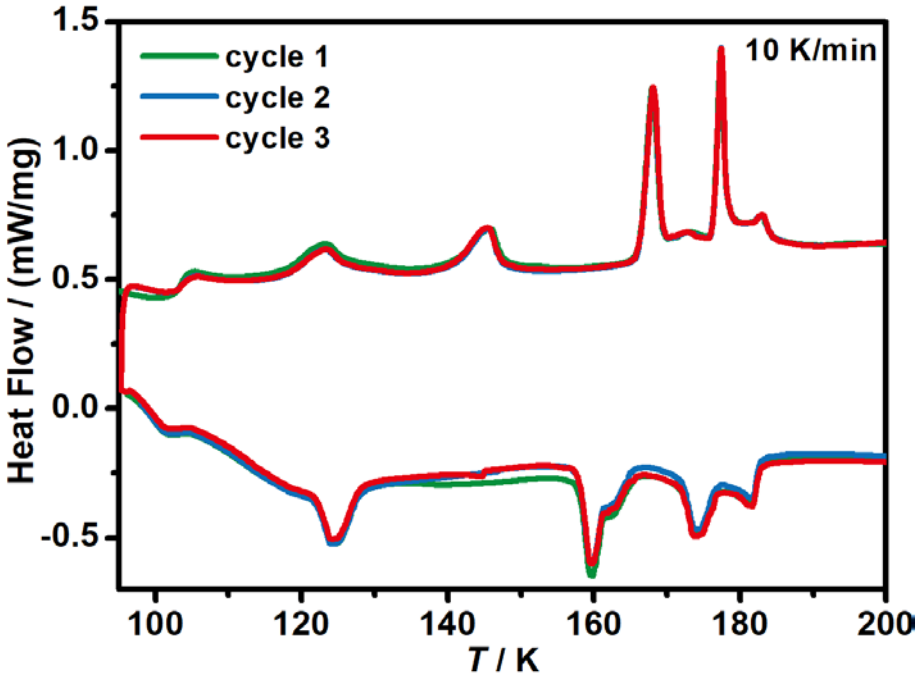


Figure S5. DSC curves with three consecutive cycles for **1Au** at 10 K min^{-1}.

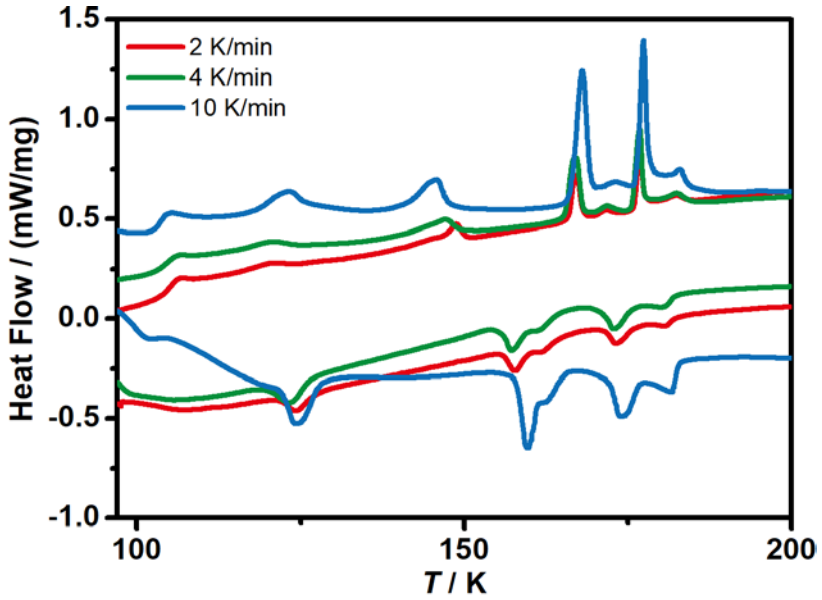


Figure S6. DSC curves for **1Au** at 2 K·min^{-1} (red), 4 K min^{-1} (green), and 10 K min^{-1} (blue).

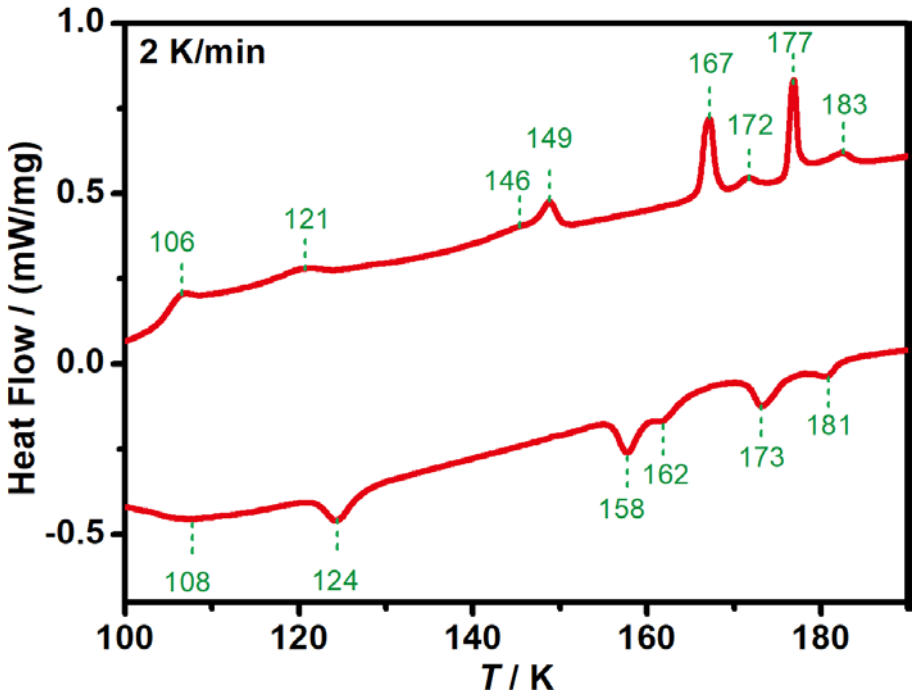


Figure S7. DSC curve for **1Au** at 2 K min^{-1}.

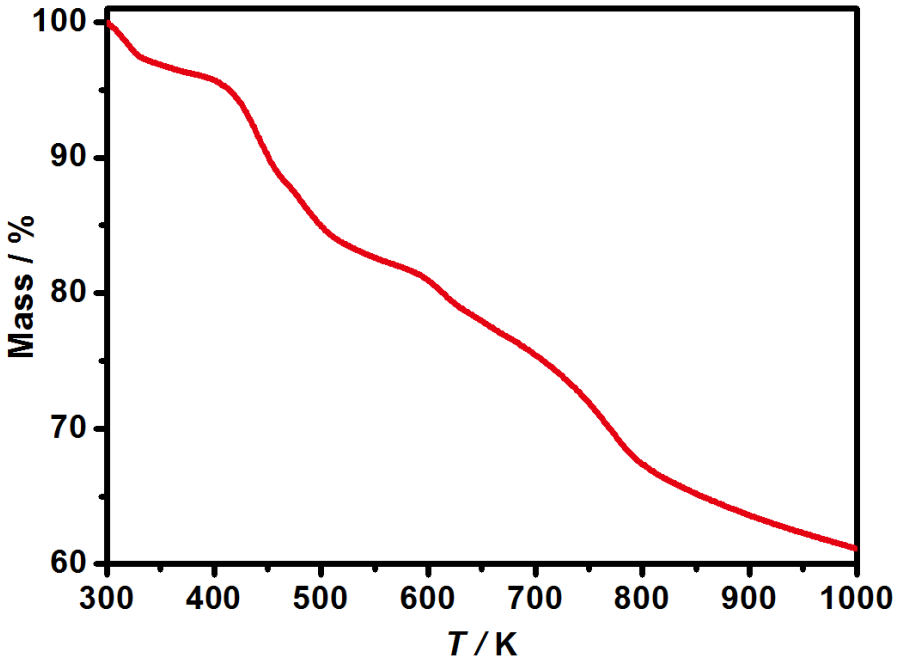


Figure S8. Thermogravimetric analysis of **1Au**.

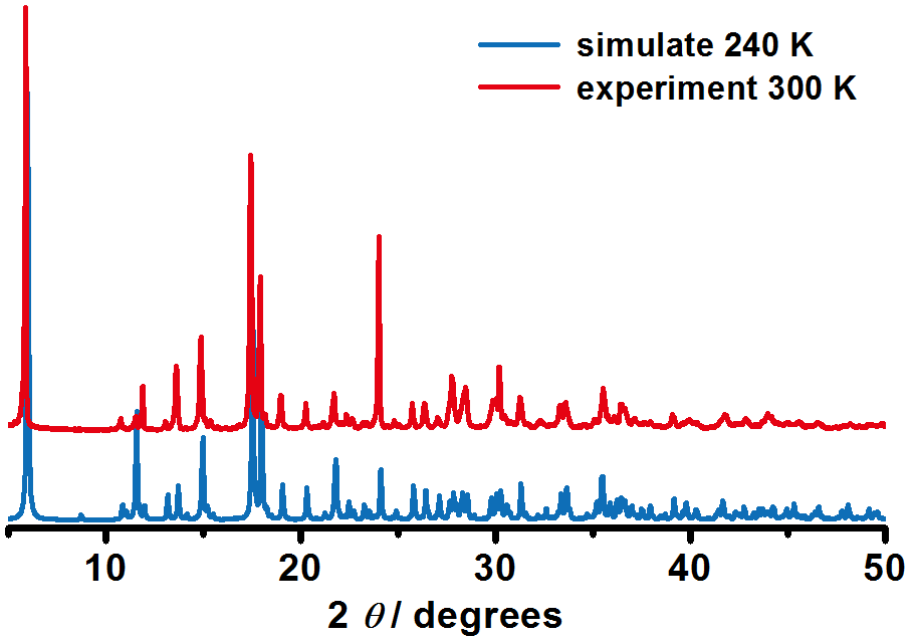
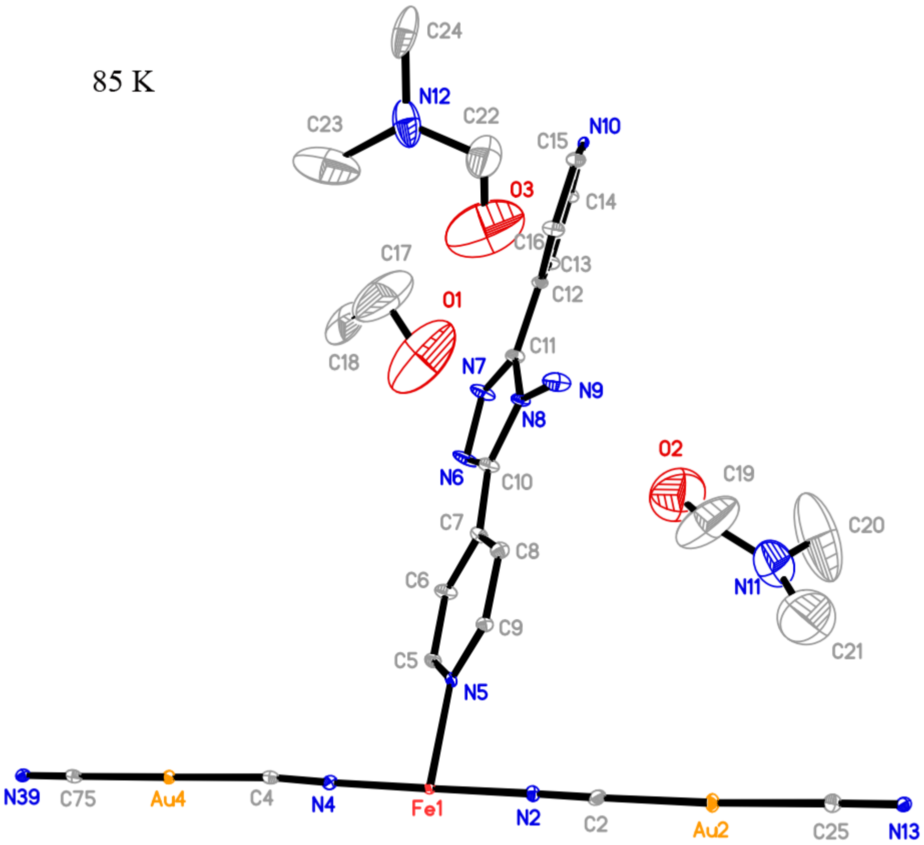


Figure S9. Powder X-ray diffraction of **1Au**.

85 K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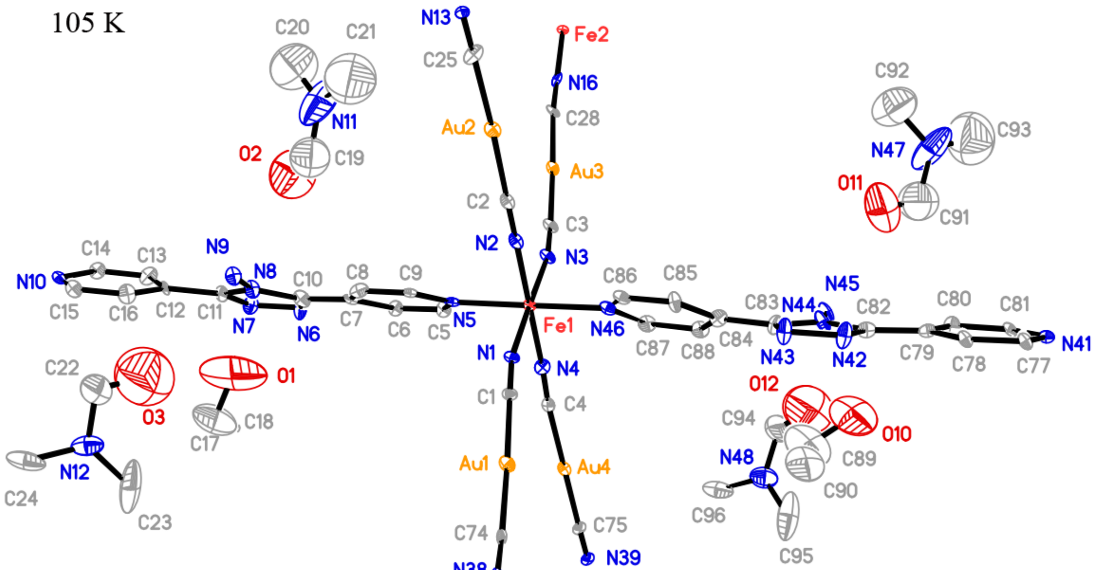
N12
C23
C22
C15
N10
O3
C14
C16
C13
C17
C12
O1
C18
C11
N7
N9
N8
O2
N6
C10
C19
C7
C20
C8
C6
N11
C9
C21
C5
N5
N39
C75
Au4
C4
N4
Fe1
N2
C2
Au2
C25
N13

105 K


N13
Fe2
C20
C21
C25
N16
N11
C28
C92
Au2
C93
O2
C19
Au3
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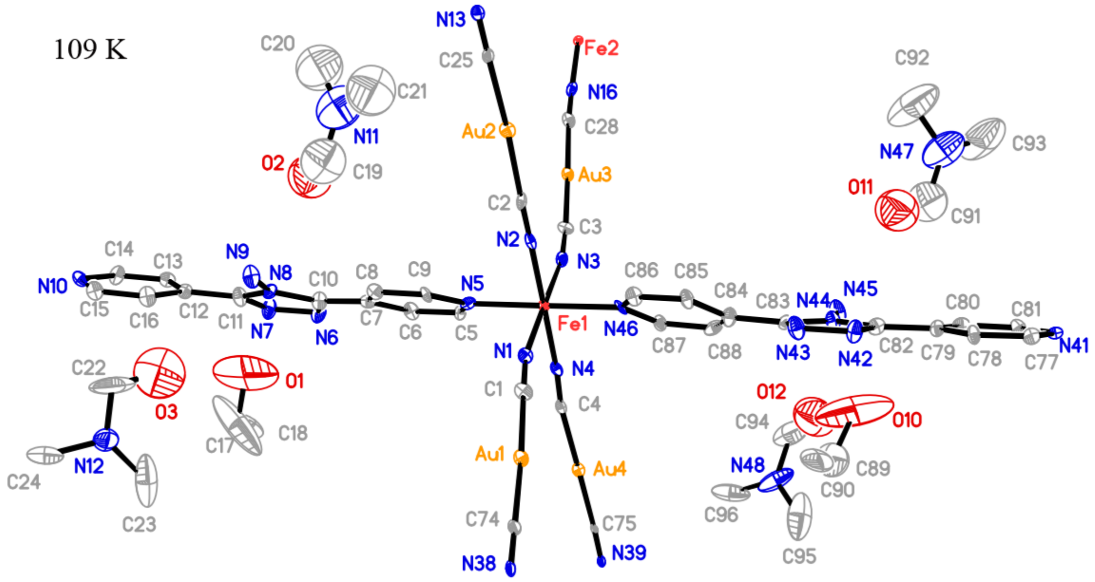
C2
C3
C91
N2
N3
C14
C13
N9
N8
C10
C8
C9
C86
C85
N45
N10
C83
N44
C82
C80
C81
C15
C16
C12
C11
N7
N6
C7
C6
C5
N5
Fe1
N46
C87
C88
C84
N43
N42
C79
C78
C77
N41
N1
N4
C22
O1
O12
O3
C18
C1
C4
C94
O10
C17
C89
N48
Au1
Au4
C90
N12
C96
C24
C23
C74
C75
C95
N38
N39

109 K



N13
C25
C20
C21
N11
O2
C19
Au2
Fe2
N16
C28
Au3
C3
C2
N2
N3
C92
N47
C93
O11
C91
C14
C13
N9
N8
C10
C8
C9
N5
C86
C85
C84
C83
N44
N45
C80
C81
N10
C15
C16
C12
C11
N7
N6
C7
C6
C5
Fe1
N46
C87
C88
N43
N42
C82
C79
C78
C77
N41
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O3
O1
C1
C4
O12
O10
C94
C17
C18
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C95
N38
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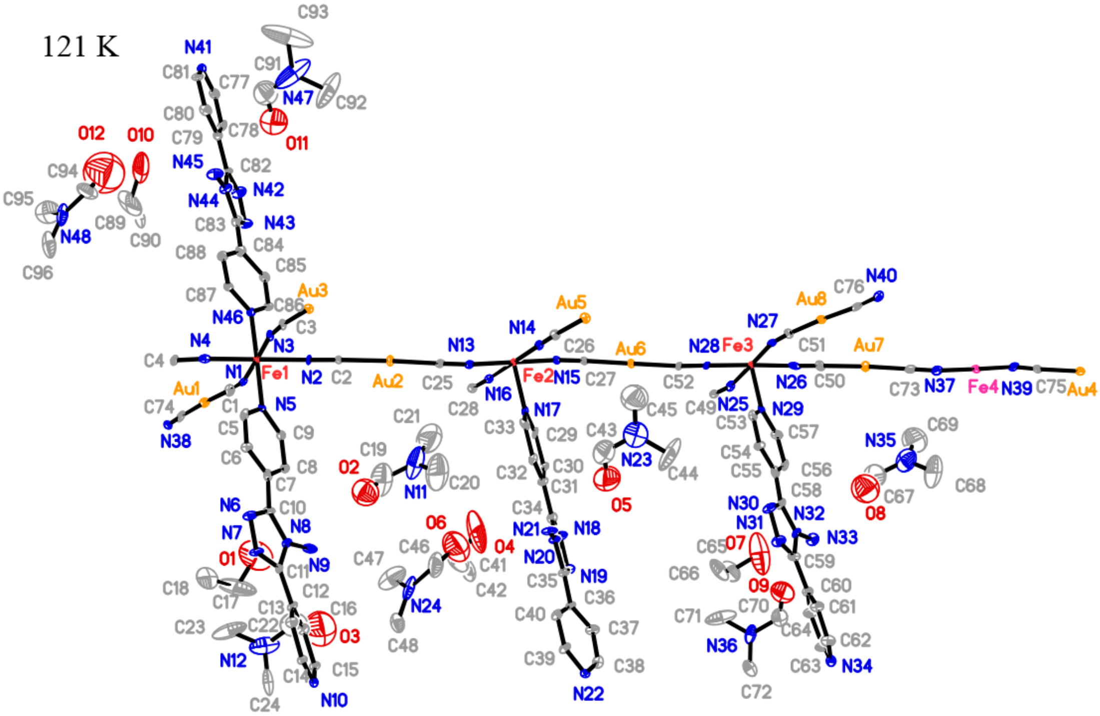
121 K



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O7
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N9
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C71
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C16
C23
C22
O3
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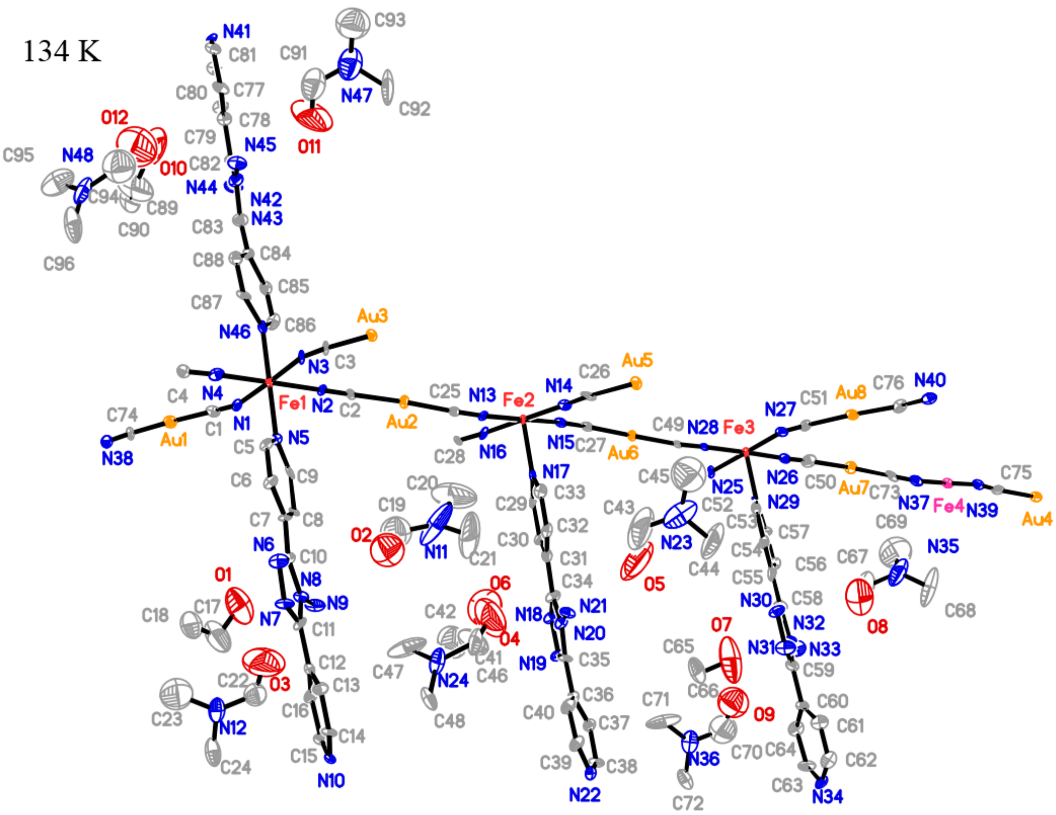
C72

134 K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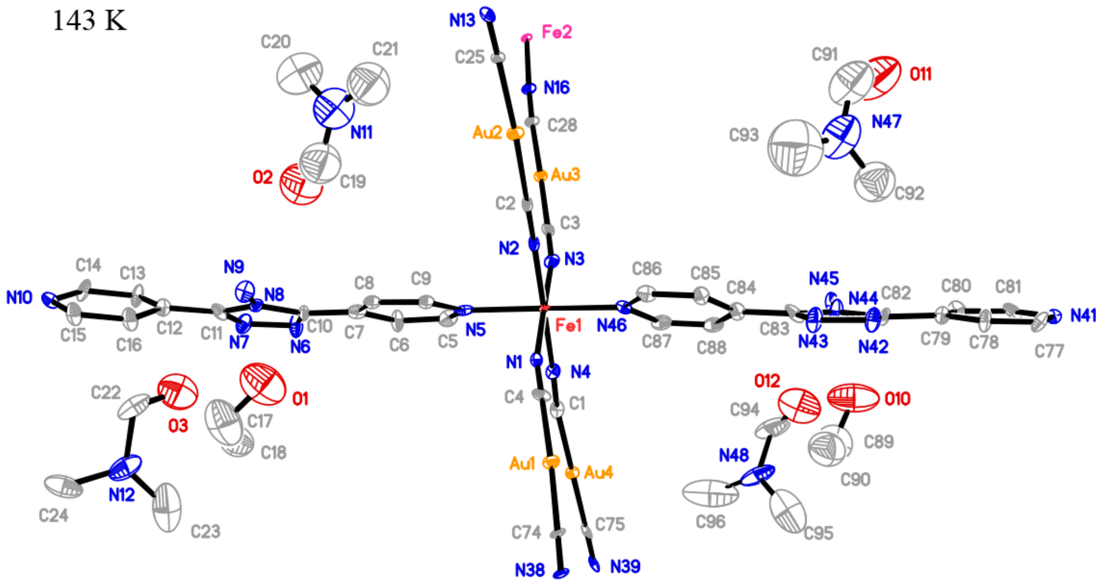
143 K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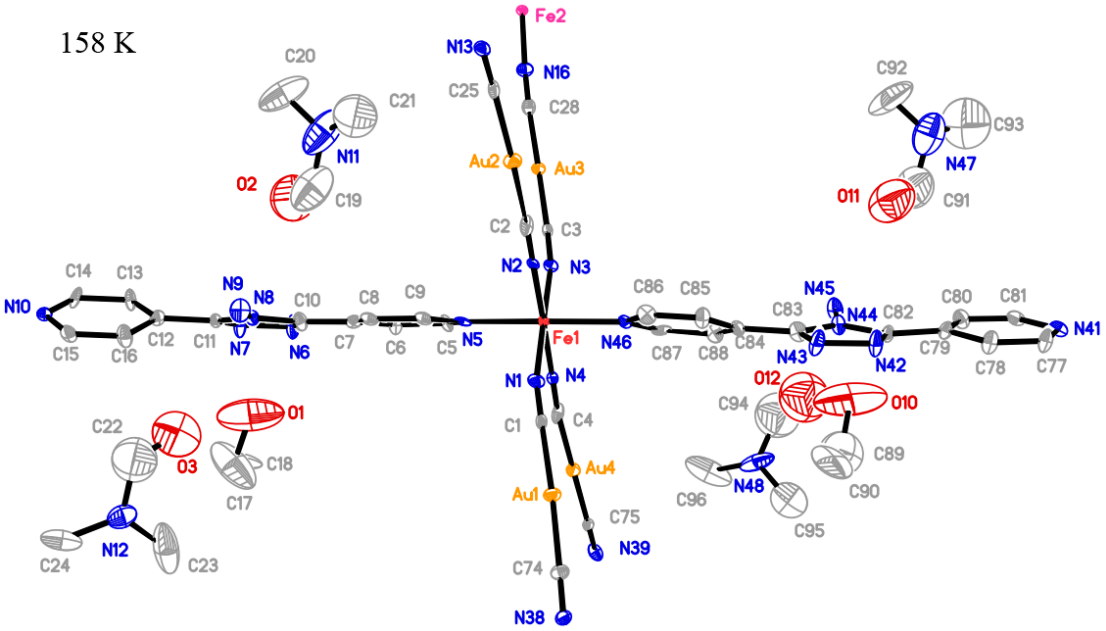
158 K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C6
C5
N5
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N45
C83
N44
C82
C80
C81
N41
C87
C88
C84
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C78
C77
C15
C16
N1
N4
C1
C4
O12
C94
O10
C89
C90
N48
C96
C95
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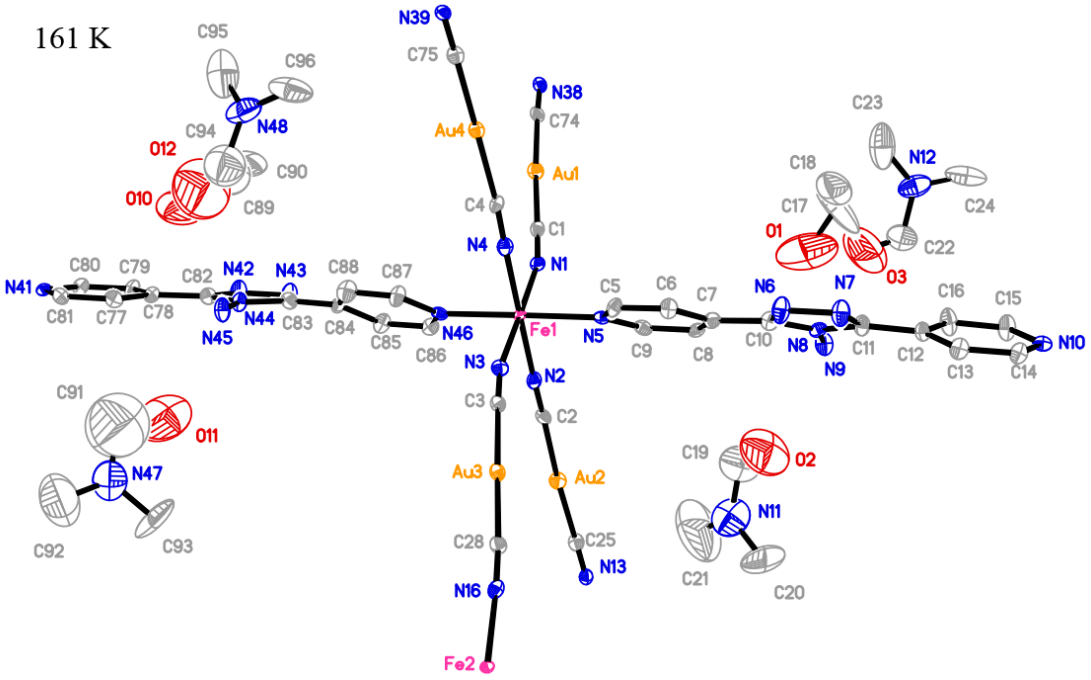
C23

161 K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N4
N1
C23
N12
C18
C24
C17
O1
O3
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C82
N42
N43
C88
C87
N41
C81
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N10
N3
N2
C3
C2
C91
O11
N47
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Au2
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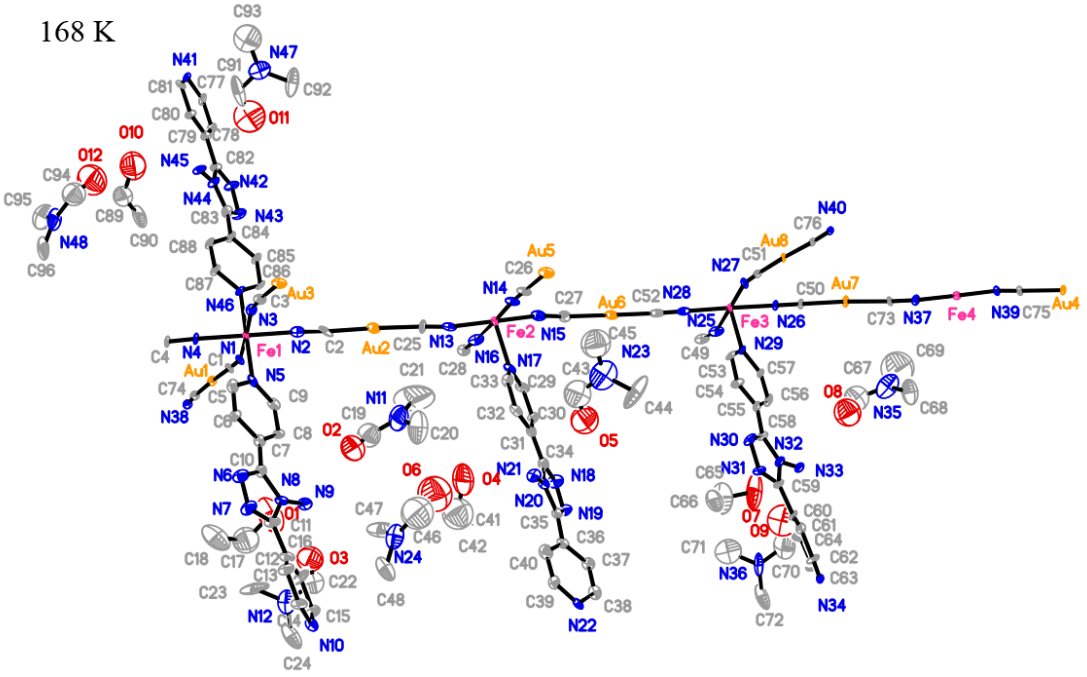
N11
C21
C20
C28
C25
N13
N16
Fe2

168 K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C86
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N46
C3
N3
Au5
C26
N14
C27
Au6
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Au8
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C51
C50
Au7
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Fe2
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O8
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C68
N38
C9
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C58
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C19
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C16
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N34
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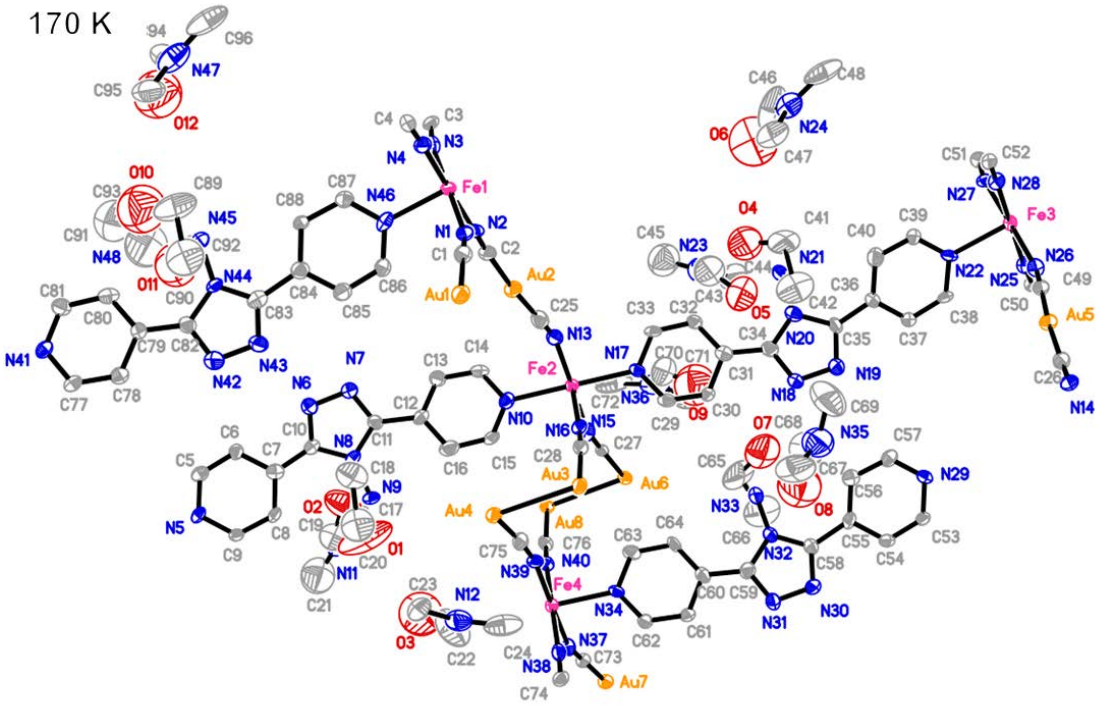
C24

170 K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O10
C89
C93
Fe1
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C88
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N45
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N2
O4
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Au8
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O1
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C59
N31
N30
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C21
C22
C24
N37
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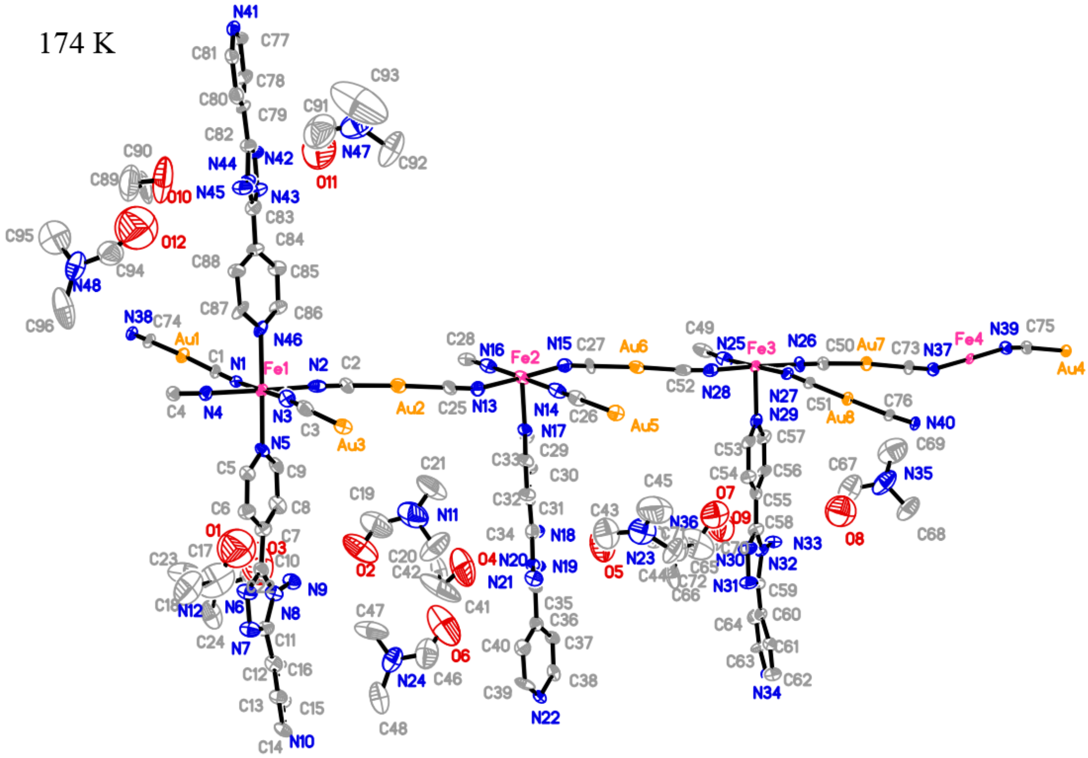
N38
Au7
C74

174 K



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C89
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N45
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Fe1
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Au4
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N4
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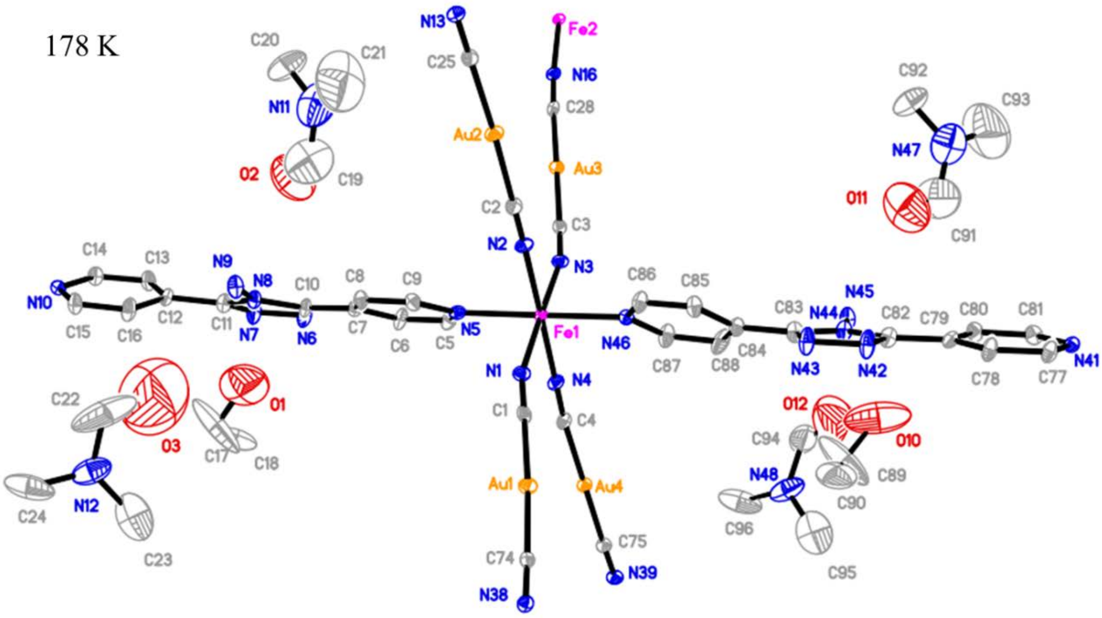
C14
N10

178 K



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Au3
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C3
O11
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N2
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C14
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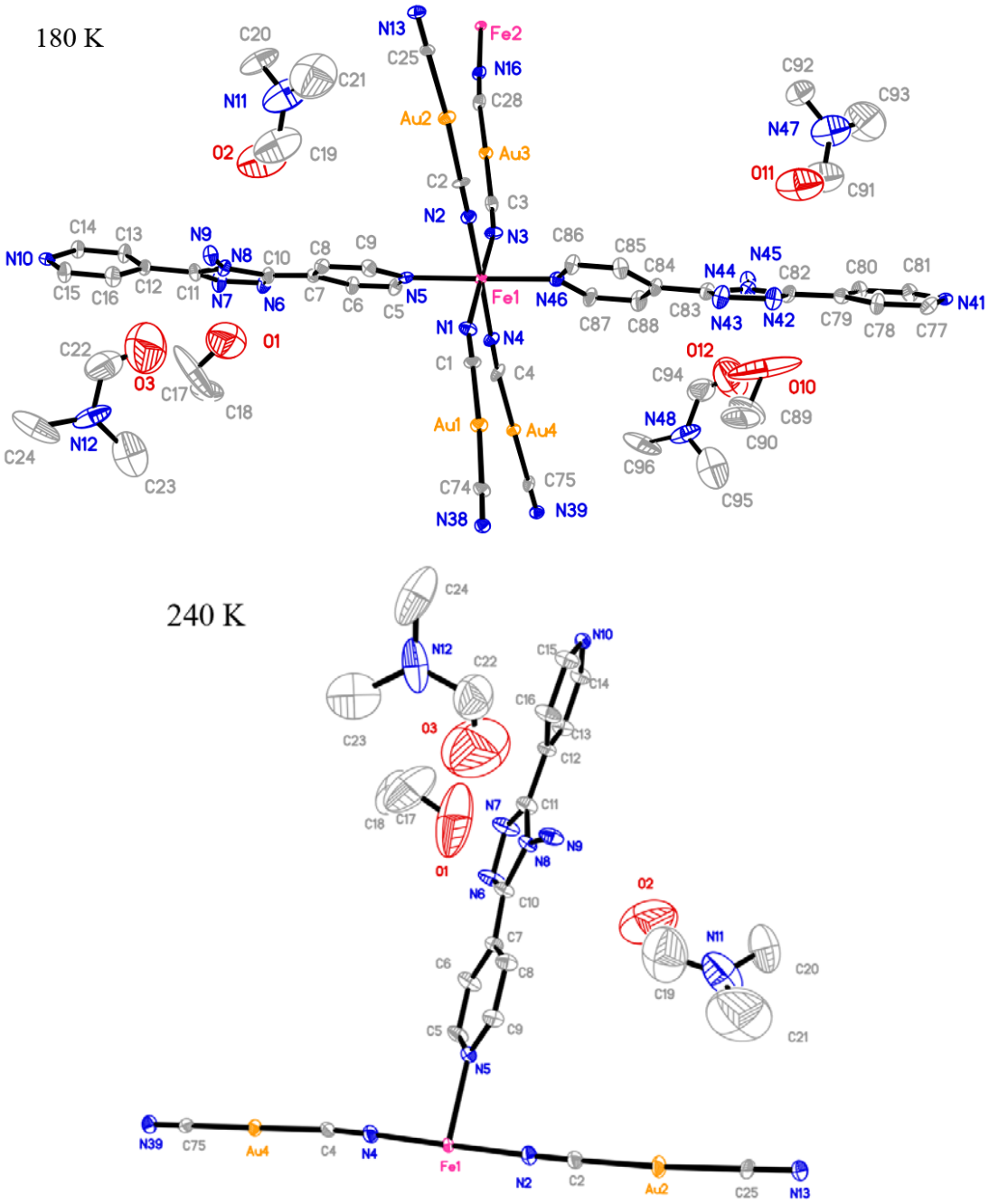


Figure S10 Asymmetric units of **1Au** at different temperatures. Thermal ellipsoids are drawn at the 30% probability. Hydrogen atoms are omitted for clarity.

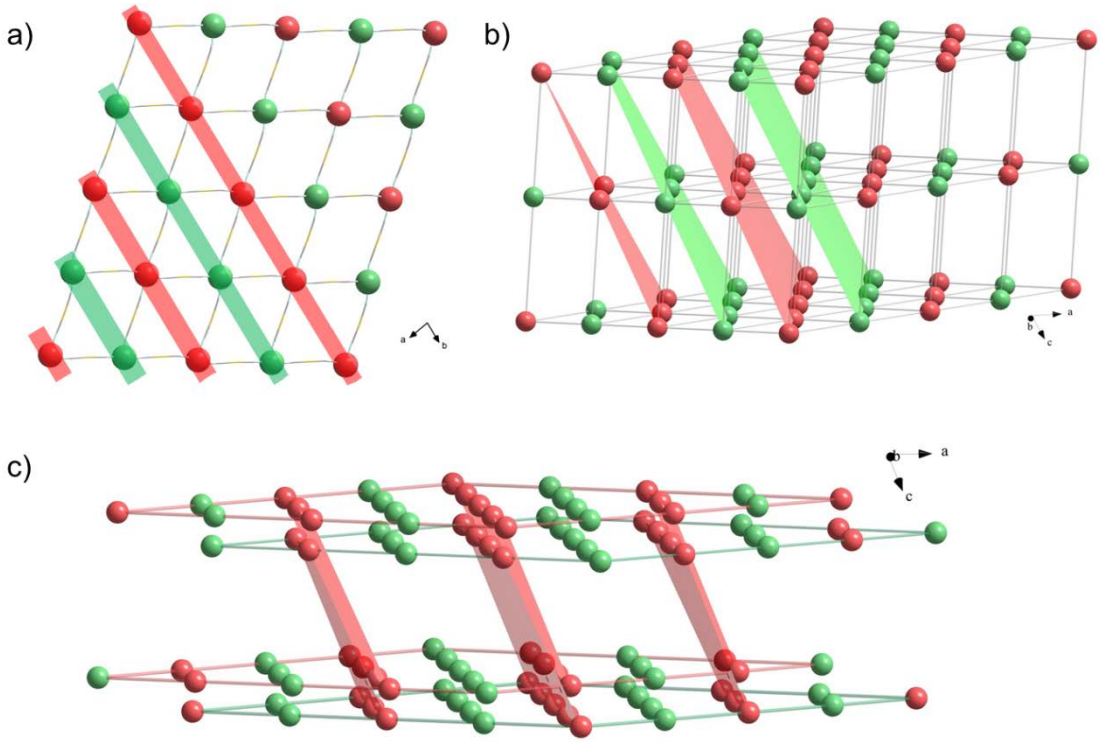


Figure S11. (a) Arrangement of two unique Fe(II) sites (Fe1, LS, green and Fe2, HS, red) within one Hofmann layer at 158 K, indicating the ordering of each Fe site along the *b*-axis. (b) View of one set of 3D framework at 158 K, indicating the ordering of each Fe site with their respective coloured blocks along the *bc* plane. (c) View of full two fold-interpenetrated 3D framework at 158 K, indicating the spin-state ordering with wave-like -LS-HS- patterning. Hofmann-type layers from two sets of 3D frameworks are indicated by green and red squares, respectively. The layers with the same colored squares are bridged by the 4-abpt ligands, which are omitted for clarity.

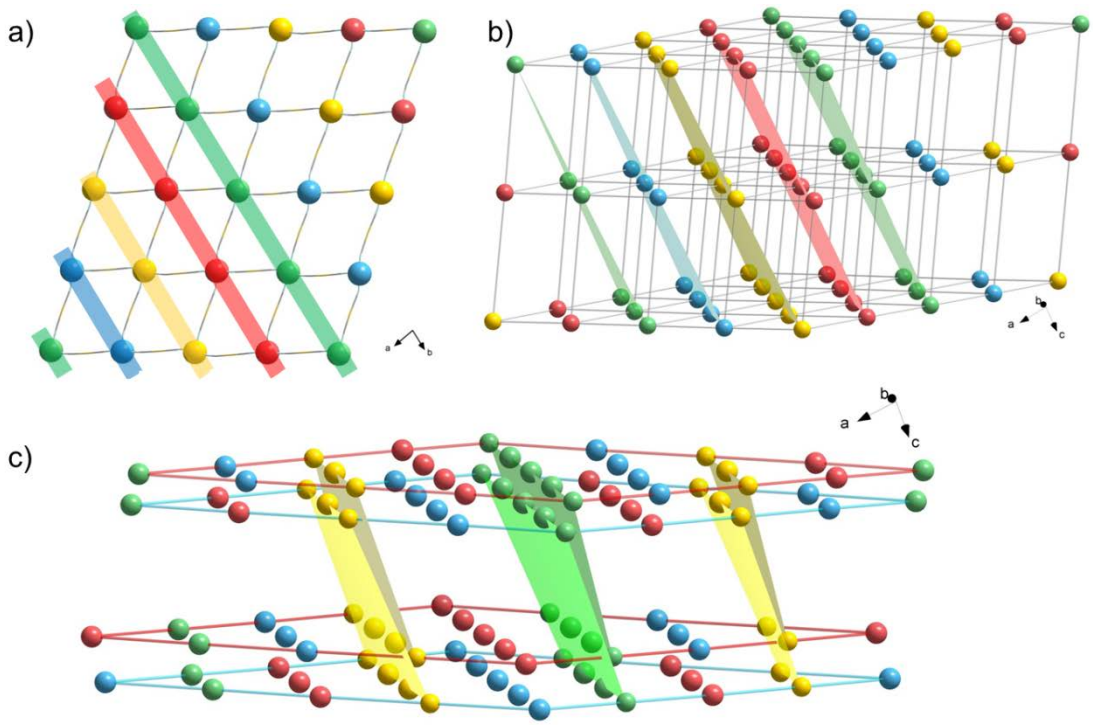
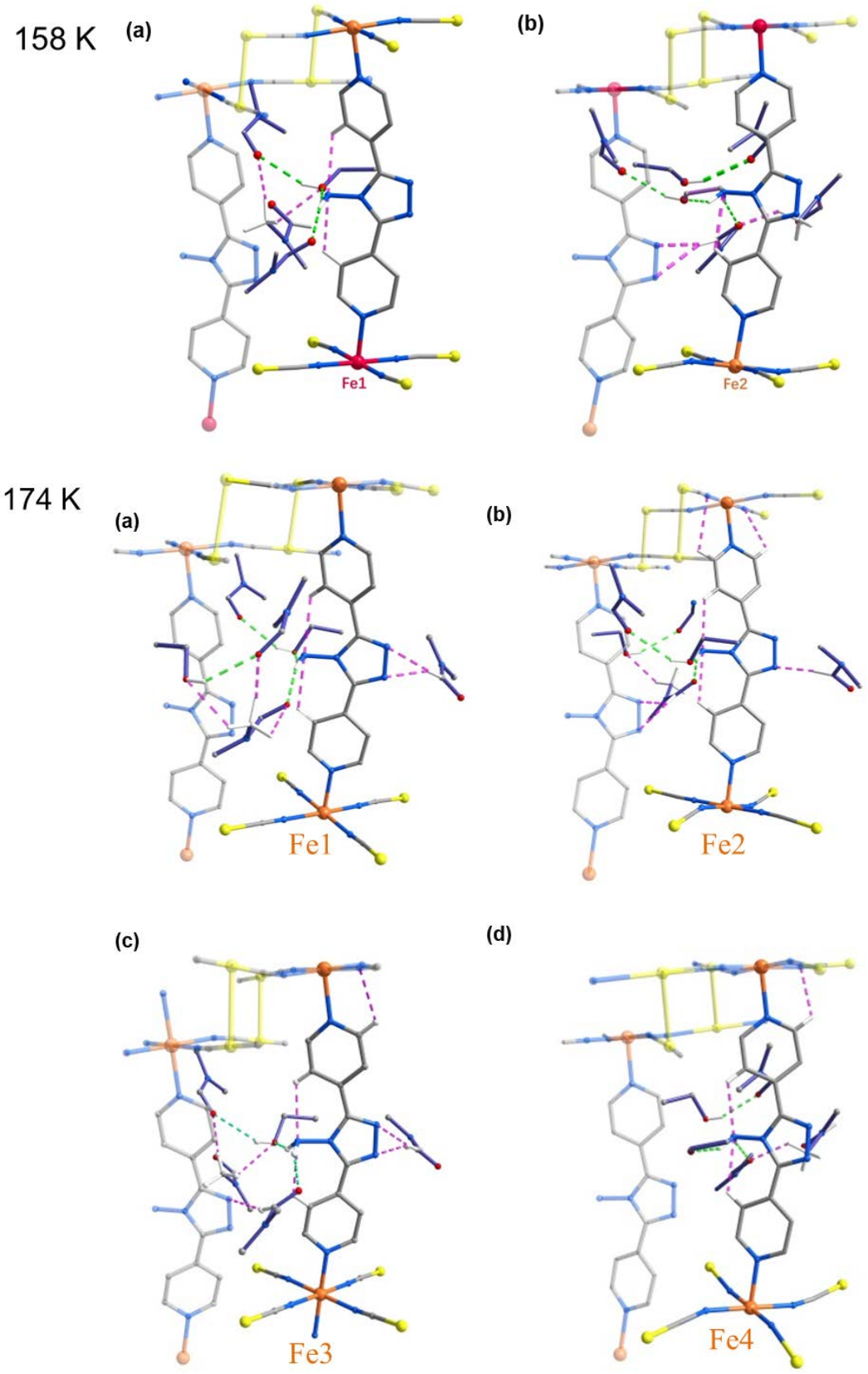


Figure S12. (a) Arrangement of four unique Fe(II) sites (Fe1, green; Fe2, red; Fe3, yellow; and Fe4, blue) within one Hofmann layer at 174 K, indicating the ordering of each Fe site along the *b*-axis. (b) View of one set of 3D framework at 174 K, indicating the ordering of each Fe site with their respective colored blocks along the *bc* plane. (c) View of full twofold-interpenetrated 3D framework at 174 K, indicating the ordering of Fe1 (green blocks) and Fe3 (yellow blocks) sites along the *bc* plane. Hofmann-type layers from two sets of 3D frameworks are indicated by red and blue squares, respectively. The layers with the same colored squares are bridged by the 4-abpt ligands, which are omitted for clarity.


158 K
(a)
Fe1
(b)
Fe2
174 K
(a)
Fe1
(b)
Fe2
(c)
Fe3
(d)
Fe4

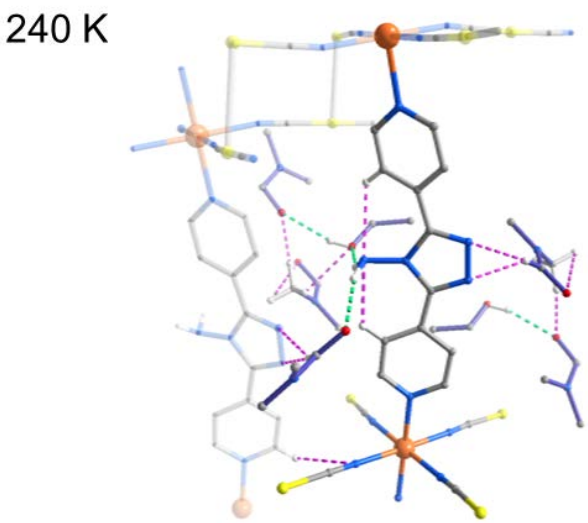


Figure S13. Hydrogen-bonding interactions in **1Au** at 158 K, 174K, and 240 K, respectively. The asymmetric unit for each 4-abpt ligand is highlighted while the others are translucent. The conventional and weak hydrogen-bonding interactions are marked by green and cyan dashed lines, respectively. Only part of Hydrogen atoms are shown while the others are omitted for clarity. Color codes: Au, yellow; N, blue; O, red; C, grey; H, white.

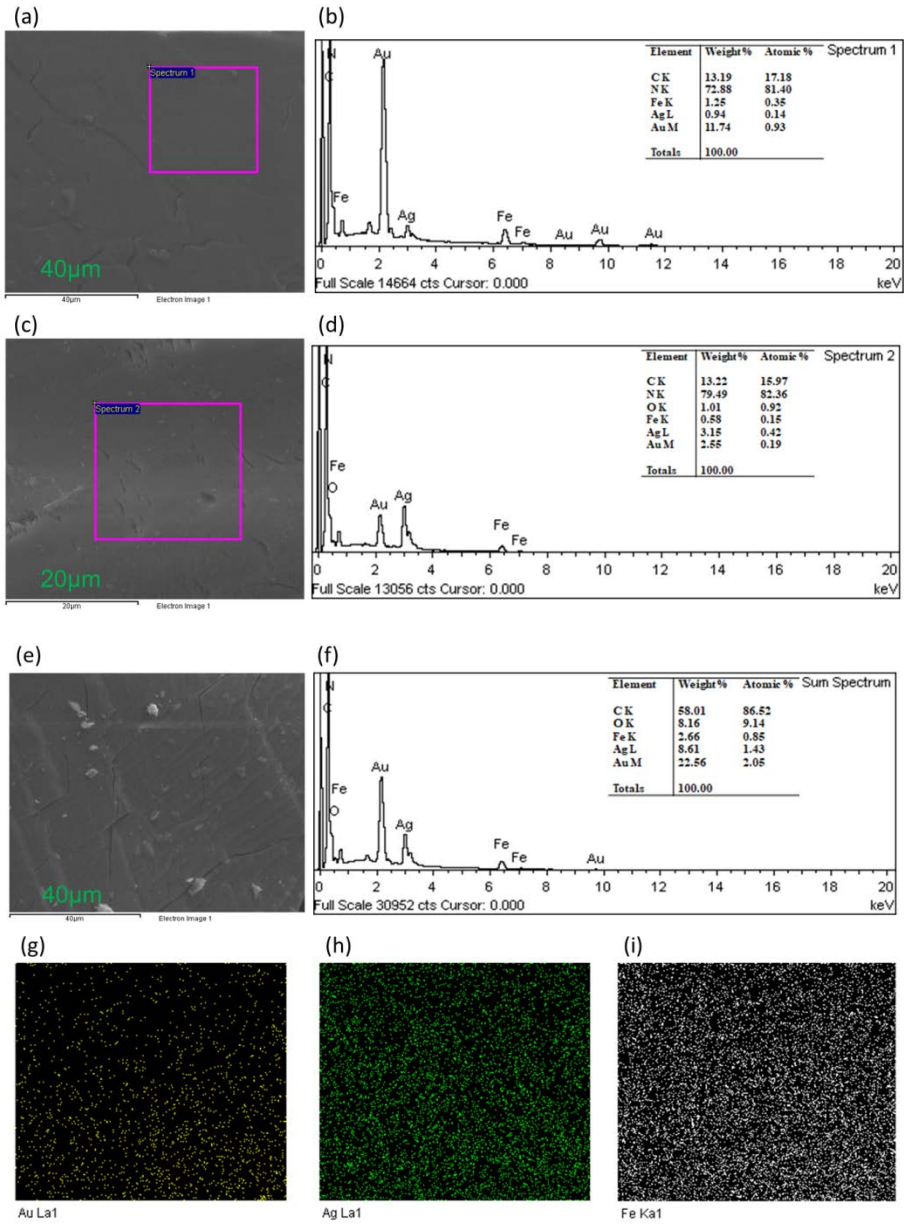


Figure S14. SEM (left) and SEM-EDS (right) spectra of **1Ag$_{0.26}$Au$_{1.74}$**, ((a) and (b)); **1Ag$_{1.38}$Au$_{0.62}$**, ((c) and (d)); **1Ag$_{0.82}$Au$_{1.18}$**, ((e) and (f)), in the form of plate crystals, after being deposited onto double-sided tape. The ratio of Ag/Au in the alloy is determined by the signal-area ratio of Ag-L/Au-M from the SEM-EDS spectrum. (g)−(i) show the SEM-EDS elemental mapping of **1Ag$_{1.38}$Au$_{0.62}$** for gold, silver, and iron, respectively.

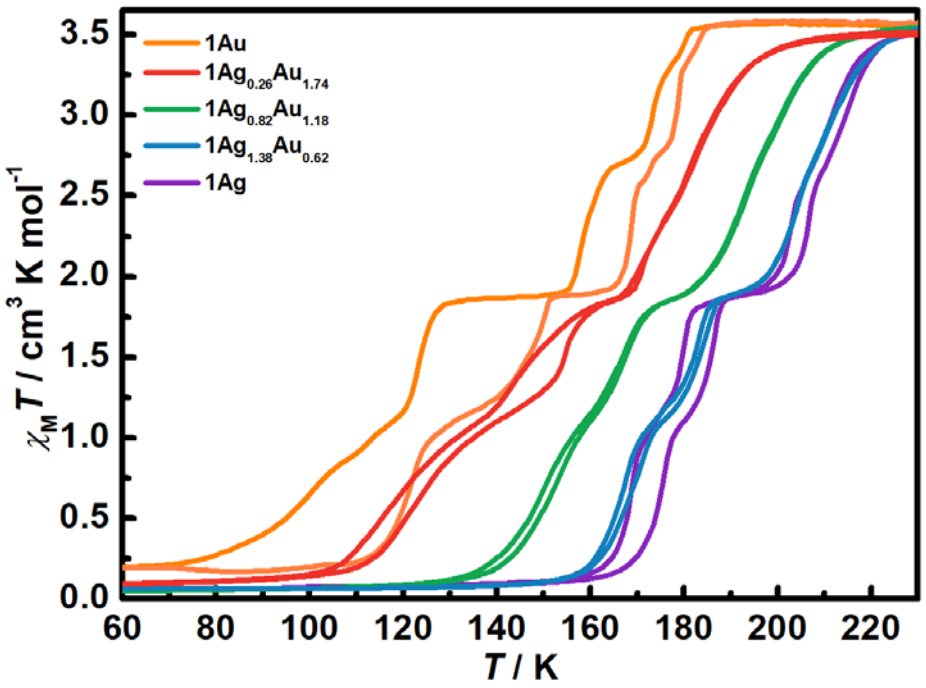


Figure S15. Thermal dependence of $\chi_M T$ at 0.5 K min^{-1} for **1Au** (orange), **1Ag$_{0.26}$Au$_{1.74}$** (red), **1Ag$_{0.82}$Au$_{1.18}$** (green), **1Ag$_{1.38}$Au$_{0.62}$** (blue) and **1Ag** (purple)